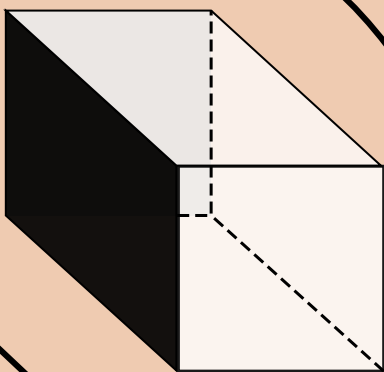A.M. VASILYEV

AN INTRODUCTION
TO STATISTICAL
PHYSICS

Based on lectures read by the author to students of the faculty of engineering electronics at the Moscow Power Engineering Institute for a number of years, the present book treats semiconductor physics with an accent placed on its application to fields associated with electronics. In these and similar fields, acquaintance with the fundamentals of statistical physics of nonequilibrium states (kinetics) is very important because a foundation is setup helping to master special subjects dealing in some way or other with the flow of an electric current in gases, semiconductors, and metals.

In acquainting the reader with the basic methods and concepts of statistical physics, the author illustrates all the material with examples, following the well-justified principle: from concrete to abstract, from simple to complicated material.

The book is intended for students of higher educational institutions who have completed a course in mathematics and general physics.

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His main interests include the physics of semiconductors and photoelectric transducers.

А. М. ВАСИЛЬЕВ

ВВЕДЕНИЕ В СТАТИСТИЧЕСКУЮ ФИЗИКУ

A. M. VASILYEV

AN INTRODUCTION TO STATISTICAL PHYSICS

Translated from the Russian by G. LEIB

PREFACE

The present book is based on lectures read by the author to students of the faculty of engineering electronics at the Moscow Power Engineering Institute for a number of years. Although statistical physics has become an essential discipline for the students of many higher technical educational establishments, to date no training aid intended especially for this category of readers has been published.

The experience I have gained in teaching the fundamentals of statistical physics has convinced me that the existing university courses are too complicated for students. They are apparently also complicated for engineers who want to improve their education. The training aids intended for higher pedagogical schools are simpler, but even they are not completely suitable. The matter is, first, that these courses widely use Hamilton's equations for deriving Liouville's theorem with whose aid the Gibbs distribution is substantiated. One reason why this path is difficult is that far from all the curricula of higher schools in theoretical mechanics provide for acquaintance with Hamilton's equations. Another reason why a special course is desired is as follows. For many professions, chiefly those associated with electronics, acquaintance with the fundamentals of statistical physics of non-equilibrium states (kinetics) is very important because a foundation is set up helping to master special subjects dealing in some way or other with the flow of an electric current in gases, semiconductors, and metals. The simpler courses do not virtually deal with kinetics.

In writing this book, I thus had in view readers whose preparation corresponds to a higher school course in mathematics and general physics.

Although the main object of the course is to acquaint the reader with the fundamental methods and concepts of

statistical physics, all the material is illustrated with examples whose practical importance is quite obvious and which are most often associated with electronics. In setting out the subject matter, I have followed the well justified principle: from concrete to abstract, from simple to complicated material.

The book makes no mention of very many important applications of statistical physics, for example, to the studying of ·magnetic phenomena or to determining the conditions of phase equilibrium. This is due first of all to the limited time allotted for studying this subject. Notwithstanding such large omissions, I am quite certain that mastering of the material treated in this book will allow the reader to freely orient himself in the broad class of important practical problems and will simultaneously prepare him for studying more difficult books in statistical physics.

The first part, devoted to the fundamentals of the theory of probability, is of an auxiliary nature and may be omitted by those readers who are acquainted with information from this field within the scope of virtually any course in the theory of probability.

The book also contains material set out in a number of training aids and monographs (see the list of recommended literature).

I am in great debt to professor V. A. Fabrikant, who looked through the manuscript, for his friendly criticism. His remarks, mainly aimed at achieving greater simplicity and clarity in treating the material, were taken into account when I prepared the final version of the manuscript.

Andrei Vasilyev

CONTENTS

INTRODUCTION

Statistical physics deals with problems that, as a rule, describe phenomena determined by the behaviour of a large number of particles. These problems are solved by using methods of the theory of probability (statistics). Statistical physics is used with great success in the most diverse branches of physics. In molecular physics, it helps to explain thermal phenomena, in electromagnetism—the dielectric, conducting, and magnetic properties of bodies, in optics it made possible the appearance of the theory of thermal radiation, of the molecular scattering of light, and so on. It is quite difficult to give a more or less complete list of the spheres in which statistical physics has found employment, moreover because recent years have seen a constant growth in the range of its applications.

In addition to matters that are of a great practical interest, statistical physics also treats problems having a fundamental, ideological significance. Not all of them have been solved completely, although as a whole statistical physics now comes forward as a science that is no less substantiated than the other branches of physics.

Statistical physics is a relatively young science. Although a number of problems, for example, the explanation of the properties of gases proceeding from the notion of molecular motion, were considered by I. Newton, D. Bernoulli, M. Lomonosov, and a number of other scientists back in the 18th century, it is evidently more correct to relate its appearance as an independent branch of physics to the second half of the 19th century.

In 1857, the German physicist R. Clausius in a publication named *On the Nature of Motion That We Call Heat* clearly indicated that heat energy is the kinetic energy of chaotic motion of molecules. The merits of introducing the concept
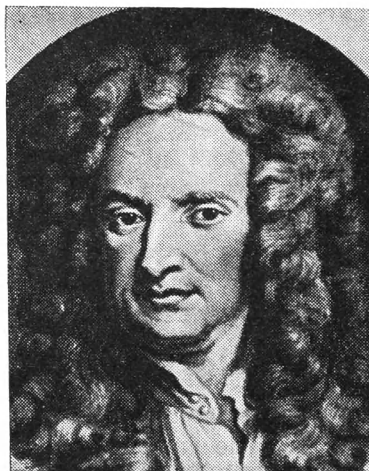
Isaac Newton
(1642-1727)

Daniel Bernoulli
(1700-1782)

of the mean free path also belong to Clausius (1859). He gave a correct molecular-kinetic explanation of the phenomena of thermal conductivity and internal friction. In 1859, a publication of the Scottish physicist J. Maxwell appeared in which he presented the law of distribution of gas molecules by velocities that now bears his name.

The further development of the molecular-kinetic theory of gases is associated with the name of the Austrian physicist L. Boltzmann. He obtained a formula describing the distribution of gas molecules in an external field (the Boltzmann distribution), and proved the theorem on the uniform distribution of kinetic energy by degrees of freedom*. Boltzmann succeeded in explaining the probabilistic meaning of entropy. Finally, we can consider as one of his main achievements the derivation of a kinetic equation (the Boltzmann equation) allowing us to describe non-equilibrium states of gases. The theorem for the function that he designated by H (the H-theorem) proved with the aid of the kinetic equation made it possible to give a statistical

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* The first information on the nature of the distribution of kinetic energy in translational motion was obtained before Boltzmann (see Smorodinsky Ya.A. *Temperature*, No. 11, Moscow, Znanie, 1977).
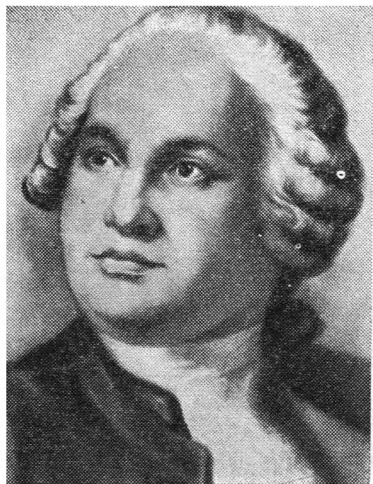
Mikhail Lomonosov
(1711-1765)

Robert Clausius
(1822-1888)

interpretation of the second law of thermodynamics. Boltzmann's views, which were attacked by many of his contemporary physicists, gained recognition only after his death in 1906.

A different approach was considered by the American mathematician and physicist J. Gibbs—a contemporary of Boltzmann. In Gibbs's works, statistical physics obtained a fundamental substantiation suitable for arbitrary systems, and not only for gaseous ones. The Gibbs distribution is treated at present as a fundamental principle whose role in statistical physics can be compared with that played by Newton's equations in classical mechanics or by Maxwell's equations in electrodynamics. Gibbs's book *Elementary Principles in Statistical Mechanics* (1902) played the same role in physics as Maxwell's *Treatise* devoted to electrodynamics.

The Gibbs distribution made it possible to relate statistics and thermodynamics in the most general way and thus complete the molecular-kinetic substantiation of this phenomenological science commenced by Boltzmann. It must be noted that certain shortcomings were detected in classical statistical physics, manifesting themselves, for
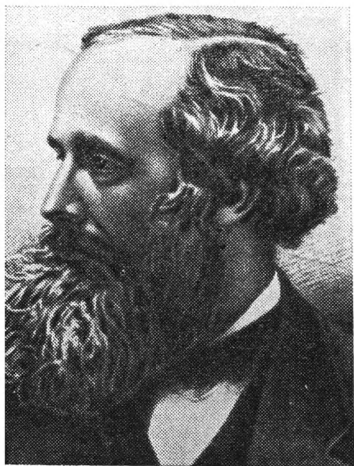
James Maxwell
(1831-1879)

Ludwig Boltzmann
(1844-1906)

instance, in the impossibility of developing a consistent
theory of thermal radiation, in the matter of the value of
the entropy (the third law of thermodynamics) and in the
unexplainability of the Gibbs paradox. They were elimi-
nated only in the next stage of development of statistical
physics associated with the appearance of quantum me-
chanics.

The theory of thermal radiation presented by M. Planck
in 1900 was the origin of quantum mechanics and success-
fully explained the properties of thermal radiation observed
experimentally. A defect of principle of the classical theory
of thermal radiation (the "ultraviolet catastrophe") was
eliminated. The Indian physicist S. Bose, considering
thermal radiation as a gas of photons, introduced in 1924
the concept of their indistinguishability, which allowed
him to obtain Planck's formula in a way differing from that
used by Planck. Later, A. Einstein developed this idea, and
the result was the creation of quantum statistics named
Bose-Einstein statistics.

A different quantum statistics appeared in 1926. It was
developed by the Italian physicist E. Fermi and by the
British physicist P. Dirac working independently of him.
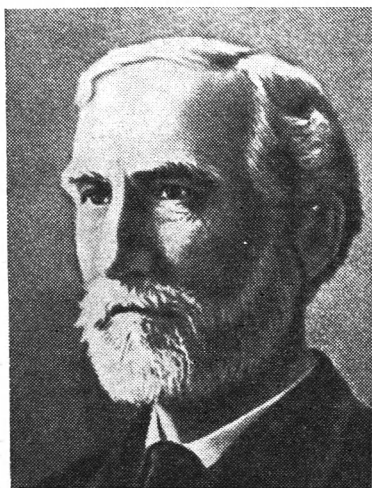
Josiah Gibbs
(1839-1903)

Max Planck
(1858-1947)
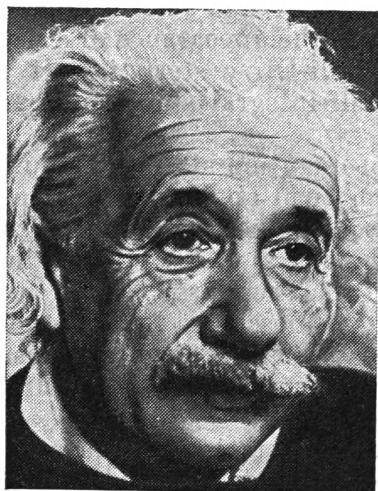
Albert Einstein
(1879-1955)

Enrico Fermi
(1901-1954)

Paul Dirac
(born 1902)
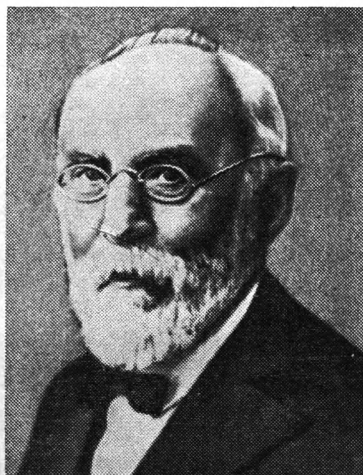
Hendrik Lorentz
(1853-1928)

The investigations of these scientists, in addition to the indistinguishability principle, took the Pauli exclusion principle into account, which led to the appearance of a new quantum statistics called the Fermi-Dirac statistics. It is applicable to particles with a half-integral spin and, particularly, to electrons.

The subsequent development of quantum statistics resulted in the appearance of a mathematical apparatus considerably differing from what is used in classical statistics. This, particularly, is associated with a way of describing the states of a system differing from the classical one.

A special class of physical systems described by a method close to the classical one includes systems known as quasi-classical. These systems are very important in the applied respect.

As we have mentioned above, the statistical theory of non-equilibrium states of gases was founded by Boltzmann, who presented his famous kinetic equation. This equation was used by the Dutch physicist H. Lorentz in his electron theory of conductance published in 1903. He proposed a simple approximate form of solution that is still in great favour at present. The rapid development of all branches

of physics in the last few decades of the present century has affected, particularly, statistical physics of non-equilibrium states that has grown up into a large and intricate branch of science.

A considerable contribution to statistical physics was also made by many outstanding Soviet scientists such as N. Bogolyubov and L. Landau.

The present book is aimed at helping those who want to master the fundamentals of statistical physics without having a special physical education. In our opinion, it is the simplest to do this by following a sequence of exposition reflecting the historical path of development of this science briefly set out above.

Part I

BASIC INFORMATION FROM THE THEORY OF PROBABILITY

Chapter 1

RANDOM EVENTS AND PROBABILITY

1.1. The Concept of Probability

All the basic concepts of the theory of probability can be illustrated by a simple example. The latter is also of independent interest in statistical physics. Consider the molecule A moving chaotically inside a vessel having the form of a box (Fig. 1.1).

A random event is defined to be a phenomenon that in an experiment set up for its observation either occurs or does not occur. For instance, the getting of the molecule A at a certain instant into the volume $\Delta\tau$ selected inside the box (Fig. 1.1) is a random event. If the molecule A could be photographed, in the picture obtained it would be either in $\Delta\tau$, when the event being considered occurred, or outside $\Delta\tau$, when the event did not occur. *An experiment involving the observation of a random event is called a trial.*

Customarily, *by the probability of a random event is meant the ratio of the number of trials m at which the given event occurred to the total number of trials M provided that M is large enough.* If we designate the probability of the event A occurring by $W(A)$, we have

$$W(A) = \frac{m}{M} \quad \text{or} \quad W(A) = \lim_{M \to \infty} \frac{m}{M}$$

Why is the requirement imposed that the number of trials M be sufficiently large? And how large must it be? The fact that M must be large is obvious already from consider-

ations of the accuracy of determining the value of the probability. Assume that we photographed the molecule in the box and stopped after obtaining the first picture showing that the molecule had gotten into $\Delta\tau$. If the total number of photographs were 127, it would be premature to arrive at the conclusion that $W(A) = 1/127$. Indeed, by making 60 more pictures, we might, for example, see that the event
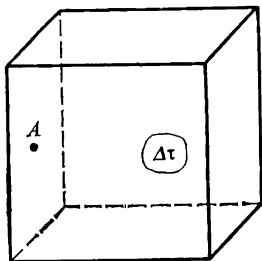
Fig. 1.1

we are interested in did not occur even once in the additional trials and, consequently, according to the new measurements the probability is 1/187. To obtain a sufficiently accurate result, we must conduct the trials until the ratios m/M will differ from one another by small values determined by the accuracy with which we want to know the probability of the event A. Strictly speaking, since the event A occurs randomly, we cannot exclude from our consideration the case in which the ratio m/M obtained experimentally does not give the correct value of the probability. Although such cases are possible in principle, they are events whose chance of occurring is extremely small, and their probability diminishes with an increasing number of trials.

We shall give an interesting historical example illustrating what has been said above. The French scientist P. Laplace, one of the founders of the theory of probability, became interested in the birth of boys and girls. The material he studied, which included data for a number of European cities, and also for France as a whole, showed that the ratio of the number of boys born m to the total number of infants born M is close to 0.5116. An analysis of the data for Paris, however, gave the value 0.5102. Taking into account that

the number of births of boys m that he had analysed was very large, Laplace arrived at the conclusion that the discrepancy he had discovered could not be a chance one. He succeeded in establishing that the number of births for Paris included abandoned infants, and the surrounding population mainly abandoned girls. After excluding the data relating to abandoned infants, the statistics of births for Paris agreed quite well with that for other cities.

The matter of how trials are conducted is also not trivial. Indeed, in the example with the molecule in the box, the trials can be run in two ways differing in principle.

In the first way, we photograph the molecule in the box consecutively at different instants. It is not difficult to see that these instants must be separated by sufficiently large intervals. If a series of photographs is taken at a very high speed, during this time the molecule will not manage to move over a considerable distance; in evaluating the ratio m/M on the basis of such a series, we shall inevitably arrive at an improper result. The intervals between the photographs must, for example, be such that the molecule will have time to travel to any other point in the box. From the experimental viewpoint, the criterion of the proper choice of the interval between photographs consists in that repeated series of trials at intervals greater than the original ones will result in the same limiting values of m/M.

In the second way of running the trial, M identical boxes are fabricated, and each of them contains a molecule of the same species A. At a definite instant, all the molecules are photographed simultaneously, and the value of the ratio m/M is established by analysing the pictures of the different boxes. *A collection of identical systems used for studying probability characteristics is called an* **ensemble**. Hence, we could use an ensemble of boxes with molecules to determine the probability.

Both ways lead to identical results if only in the first one the condition of sufficient time intervals between the trials is maintained, and in the second way all the systems of the ensemble are indeed strictly identical.

It follows from the definition of probability that its values are confined between 0 and 1. Indeed, m and M are positive numbers and, in addition, the minimum possible value of the number m is 0, and its maximum possible value equals

the total number of trials M. *An event that occurs in every trial and whose probability is therefore unity is called* **certain**. An example is the event consisting in the detection of the molecule A, known to be placed into the box, somewhere inside the latter. It is natural that in each picture of the entire box the molecule A will be detected, i.e. this event occurs in each trial and, consequently, is certain. In the opposite case, when an event cannot take place even in a single trial and, therefore, its probability is zero, it is called **impossible**. We can give as an example the event consisting in that the molecule A will not be detected in the box: if the molecule is in the box, this event is impossible.

1.2. Set of Mutually Exclusive Events

Of great significance in the construction and application of the theory of probability is the concept of a set of **mutually exclusive** events.

Two events are said to be mutually exclusive *if the happening of one excludes the possibility of happening of the other.* Con-

(a)   (b)
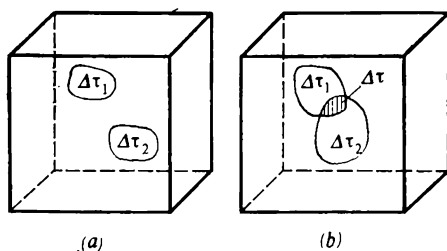
Fig. 1.2

sider an example. Two volumes, $\Delta\tau_1$ and $\Delta\tau_2$, are selected in the box chosen for observing the molecule A. If the volumes do not intersect, as is shown in Fig. 1.2a, the event *1* consisting in that at the instant t the molecule A will be in $\Delta\tau_1$ and the event *2* consisting in that at the same instant t it will be in $\Delta\tau_2$ are mutually exclusive. It is evident that when the two volumes intersect (Fig. 1.2b) the same two events are compatible because getting of the molecule at

the instant t into the hatched region of intersection $\Delta \mathbf{v}$ signifies that it is simultaneously in both volumes.

The applied value of the concept of mutually exclusive events is due to the following theorem: *the probability of happening of one of two mutually exclusive events equals the sum of the probabilities of happening of each of them.* This theorem is easily proved when considering the example given above. Assume that getting of the molecule into the first of the two non-intersecting volumes is characterized by the probability

$$W\,(1) = \frac{m_1}{M}$$

where m_1 is the number of times the molecule got into the first volume in M trials. Similarly, the probability of the molecule getting into the second volume is

$$W\,(2) = \frac{m_2}{M}$$

The event consisting in that the molecule gets into at least one of the two volumes happened $m_1 + m_2$ times. Now in accordance with the general definition, we can find that the probability of happening of at least one of the two events is

$$W = \frac{m_1 + m_2}{M} = \frac{m_1}{M} + \frac{m_2}{M} = W\,(1) + W\,(2)$$

and this proves the theorem. With **compatible** events (intersecting volumes), we cannot assert that the number of times the molecule gets into the first or the second volume equals $m_1 + m_2$. This number will be smaller because there are cases when the molecule gets into the intersection of the volumes, and such events are included simultaneously in m_1 and m_2.

  A complete set of mutually exclusive events is defined to be such a set of them in which the happening of one is certain. The mutually exclusive events considered in the preceding example (Fig. 1.2a) do not form a complete set because the molecule may be outside both volumes $\Delta \tau_1$ and $\Delta \tau_2$, i.e. a situation is possible when none of them occurred. If, however, we supplement the events *1* and *2* with the event *3* consisting in that the molecule will be detected inside the box in the space remaining after the subtraction of $\Delta \tau_1$

and $\Delta\tau_2$, the new group of three events will form a complete set. Indeed, since the volumes do not intersect, the events are mutually exclusive; in addition, the happening of any one of them is certain because the molecule is either in $\Delta\tau_1$, or in $\Delta\tau_2$, or outside them.

Events are said to be equally possible if the probability of any of them happening has the same value. To explain this concept, we shall assume that a box is divided into two
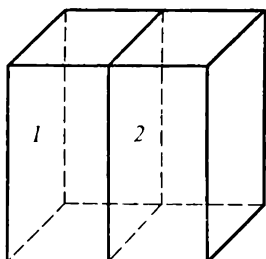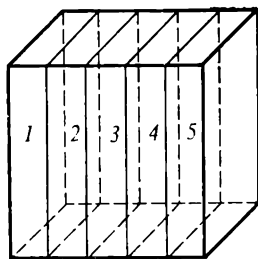
Fig. 1.3   Fig. 1.4

equal parts *1* and *2* (Fig. 1.3) and consider a set consisting of two events: the getting of the molecule *A* into *1* and its getting into *2*. The volumes do not intersect, and, consequently, the events are mutually exclusive. The set is complete because the volumes *1* and *2* completely exhaust the volume of the box. Finally, from the complete equivalence of the two volumes, it is evident that the probability of getting into *1* equals that of getting into *2*. In this example, the events *1* and *2* thus form a complete set of mutually exclusive equally possible events. We must stress that the conclusion on the events being equally possible is supported by quite specific physical notions of the nature and conditions of motion of the molecule. For example, if the molecule has a magnetic moment and a magnet that produces a non-homogeneous magnetic field is placed at the left wall of the box, the probability of detecting the molecule in the volume *1* will be higher, i.e. the events are not equally possible.

Figure 1.4 shows five volumes of identical size into which a box has been mentally divided. Are the events corresponding to the molecule getting into each of them equally

possible? The reply depends on the conditions that occur when the molecule collides with a wall. If we assume that the molecule upon colliding with a wall adheres for some time to the latter, it will naturally spend more time in volumes *1* and *5*. Consequently, the probabilities $W(1)$ and $W(5)$, although they are equal to each other, are greater than the others. The conditions of motion in each of the volumes *2*, *3*, and *4*, however, are absolutely identical, and therefore the probabilities $W(2)$, $W(3)$, and $W(4)$ are equal to one another. In a real situation, conditions most often occur in which collisions with a wall occur so that
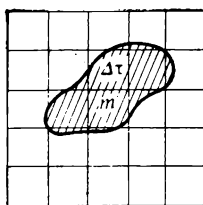
Fig. 1.5

they are equivalent to a perfectly elastic impact. The probabilities of all five events here will be the same. In the following, we shall always have in view exactly such a nature of collisions, so that *events consisting in detection of a molecule at a certain instant t in equal volumes are equally possible*.

The value of the concept of a complete set of equally possible mutually exclusive events consists in that it allows us to find the value of the probability of an event theoretically. Consider the example of determining the probability of the fact that the molecule will be within the volume $\Delta\tau$ inside the box.

We mentally divide the box into n identical parallelepipeds (Fig. 1.5) of such a small size that the volume $\Delta\tau$ with a high accuracy can be formed from a certain number m of them. As we have shown above, the events consisting in that at the instant t the molecule A will be in one of the parallelepipeds form a complete set of mutually exclusive equally possible events. The probability of the molecule A

being in a definite parallelepiped is the same for all the parallelepipeds (the condition of equal possibility) and can be found from the condition of the completeness and mutual exclusiveness of the events in the set. The probability that the molecule A is inside the vessel is unity (a certain event). On the other hand, according to the rule of addition of probabilities of mutually exclusive events, the same probability can be represented as the sum of the probabilities of all the events in the set, i.e. $1 = nW$. It thus follows that

$$W = \frac{1}{n}$$

The probability $W(\Delta\tau)$ we are interested in equals the sum of the probabilities of the molecule getting into any of the parallelepipeds forming $\Delta\tau$. Since their total number is m, by again using the theorem of addition, we find

$$W(\Delta\tau) = m \times \frac{1}{n} = \frac{m}{n} \qquad (1.1)$$

If we multiply the numerator and the denominator by the volume of one parallelepiped, we obtain $\Delta\tau$ in the numerator, and the volume of the entire box in the denominator. Consequently, *the probability of the fact that a molecule in a vessel of volume V will be in the element $\Delta\tau$ of the volume at the instant t is*

$$W(\Delta\tau) = \frac{\Delta\tau}{V} \qquad (1.2)$$

Formula (1.2) does not contain the number of parallelepipeds n, so that the final result does not depend on the size of the volumes into which we mentally divided the volume of the vessel. They may be considered infinitely small and, consequently, will exactly form the volume $\Delta\tau$ so that the formula (1.2) is absolutely accurate, unlike the approximate formula (1.1).

1.3. Independent Events

In calculations which we have to perform with probabilities, the property of the **independence** of random events is frequently used. *Two events are said to be independent if*

*the happening of one of them does not affect the probability
of happening of the second one.* Consider an example. Let
the first event consist in that the molecule A gets into the
volume $\Delta\tau_1$ at the instant t, and the second, in that another
molecule B gets into the volume $\Delta\tau_2$ at the same instant.
If regardless of whether or not the molecule A got into $\Delta\tau_1$,
the probability of the molecule B getting into $\Delta\tau_2$ equals
the same quantity $\Delta\tau_2/V$, the events are independent. This
is how matters will be if the molecules do not interact with
each other. In this case, even if the volumes $\Delta\tau_1$ and $\Delta\tau_2$
coincide, the events are independent. The presence of inter-
action, however, will change matters. For instance, upon
the mutual repulsion of the molecules, the probability of
the molecule B appearing in the volume $\Delta\tau_1$ together with
A is lower than in the absence of A. In actual conditions,
all molecules interact with one another, but the forces of
interaction diminish very rapidly with an increasing dis-
tance between them, so that at distances of the order of
several diameters of the molecules the interaction may be
disregarded completely. This makes it possible at low con-
centrations (gases), when the mean distance between mole-
cules is much greater than their diameter, to consider that
the events treated in the above example are independent.
At large concentrations (greatly compressed gases, liquids),
matters are different.

*The probability of the joint happening of independent
events equals the product of the probabilities of each of them.*

To explain this property, we shall consider a rarefied gas.
Assume that upon n trials the molecule A was found m_1
times in the volume $\Delta\tau_1$, and the molecule B was found m_2
times in the volume $\Delta\tau_2$, i.e.

$$W(A) = \frac{m_1}{n} \text{ and } W(B) = \frac{m_2}{n}$$

Of all the trials whose total number is m_1 in which A got
into $\Delta\tau_1$, let us set aside the ones in which B also got into
$\Delta\tau_2$. Since the probability of the event B happening is m_2/n,
the number of events set aside must equal $m_1\,(m_2/n)$. If
we now relate the found number of events to the total num-
ber of trials, the probability of the joint happening of the

events A and B is

$$W(AB) = \frac{m_1(m_2/n)}{n} = \frac{m_1}{n}\frac{m_2}{n} = W(A)W(B)$$

This formula is the mathematical expression of what has been said above.

1.4. Conditional Probability

The question appears: how can we determine the probability of the joint happening of two dependent events? To answer it, let us again turn to an example. We take as the event *1* the getting of the molecule A into the volume $\Delta\tau_1$ at the instant t, and as the event *2* the getting of the same molecule into the volume $\Delta\tau_2$ at the same instant t. These events are dependent. Assume, for instance, that the volumes $\Delta\tau_1$ and $\Delta\tau_2$ do not intersect, i.e. that the events *1* and *2* are mutually exclusive. Now, if the molecule got into $\Delta\tau_1$, it could not, naturally, be at the same instant in $\Delta\tau_2$. Hence, if the probability of the event *2* is $\Delta\tau_2/V$, the same probability, provided that event *1* happens, equals 0. It is exactly the change in the value of the probability of the event *2* because of the happening of the event *1* that signifies the **dependence** of these events in the probabilistic meaning.

In the more general case of arbitrarily intersecting volumes $\Delta\tau_1$ and $\Delta\tau_2$, the events *1* and *2* are also dependent. To convince ourselves that this is true, let us calculate how the probability of the event *2* changes provided that the event *1* happened. The occurrence of the event *1* signifies that the molecule has gotten into the volume $\Delta\tau_1$, and therefore it can be considered as a new vessel containing the molecule. The probability of detecting the molecule at the same instant in $\Delta\tau_2$ is the probability of the fact that it will be in the volume $\Delta\tau$, which is a common part of $\Delta\tau_1$ and $\Delta\tau_2$ (see Fig. 1.2b). This probability equals the ratio of $\Delta\tau$ to the volume of the "new vessel" $\Delta\tau_1$. Hence, the probability $W(2)$ of the event *2* without the condition *1* or, as is said, the **unconditional probability**, has the value

$$W(2) = \frac{\Delta\tau_2}{V}$$

while *the conditional probability* $W_1(2)$ *is the probability of the event 2 provided that the event 1 happened*; in the given

case it is

$$W_1(2) = \frac{\Delta\tau}{\Delta\tau_1}$$

It is obvious that in the general case the conditional and unconditional probabilities do not coincide in value, and this is just what signifies the dependence of events on one another. For independent events, the conditional and unconditional probabilities are equal.

We can now formulate an almost evident rule. *The probability $W(1, 2)$ of the joint happening of the two events 1 and 2 equals the probability $W(1)$ of the event 1 multiplied by the conditional probability $W_1(2)$, or the probability $W(2)$ of the event 2 multiplied by the conditional probability $W_2(1)$.* This is written mathematically as follows:

$$W(1, 2) = W(1)\, W_1(2) = W(2)\, W_2(1)$$

Let us take an example with two intersecting volumes to illustrate this rule. The probability $W(1, 2)$ of getting into both *1* and *2* is, in essence, the probability of getting into the intersection of these two regions, i.e. into $\Delta\tau$, so that

$$W(1, 2) = \frac{\Delta\tau}{V} \qquad (1.3)$$

Formula (1.3) can be written either in the form

$$W(1, 2) = \frac{\Delta\tau}{V} = \frac{\Delta\tau}{\Delta\tau_1}\,\frac{\Delta\tau_1}{V} = W(1)\, W_1(2)$$

or in the form

$$W(1, 2) = \frac{\Delta\tau}{V} = \frac{\Delta\tau}{\Delta\tau_2}\,\frac{\Delta\tau_2}{V} = W(2)\, W_2(1)$$

which completely conforms to the general statements made above.

1.5. Binomial Distribution of Probabilities

The information given above allows us to solve many problems of statistical physics. In the present section, we shall consider one of them having great significance both from the viewpoint of application and from that of development of the probability theory itself.

Assume that a vessel contains a gas with a total number of molecules equal to N. Let us mentally separate a part of the volume of the vessel $\Delta\tau$ and determine the probability of finding n molecules in $\Delta\tau$. The solution of this problem will make it possible, particularly, to indicate the probability of a certain value of the density of a gas, which is of interest for some physical applications.

Let us begin with the case of two molecules ($N = 2$) and assign the numbers *1* and *2* to the molecules. To determine the probability we are interested in, we can consider the following complete set of mutually exclusive events:

(1) the molecules *1* and *2* are in $\Delta\tau$;
(2) the molecule *1* is in $\Delta\tau$, and *2* is outside this volume;
(3) the molecule *2* is in $\Delta\tau$, and *1* is outside it;
(4) both molecules are outside $\Delta\tau$.

The probabilities of these events are evaluated as follows.

The probability of the molecule *1* being in $\Delta\tau$ is $W = \Delta\tau/V$, while the probability of its being outside this volume is

$$1 - W = 1 - \frac{\Delta\tau}{V}$$

because the sum of the probabilities of both events must be unity. The relevant probabilities for the molecule *2* have the same values. Let us now turn to the first event when both molecules are in $\Delta\tau$. Since it is assumed that the interaction of the molecules may be disregarded, the getting of the molecules *1* and *2* into $\Delta\tau$ are independent events, and therefore the probability W_1 of the first event is the product of the probabilities of the molecules *1* and *2* getting into $\Delta\tau$, i.e.

$$W_1 = \frac{\Delta\tau}{V}\,\frac{\Delta\tau}{V} = \left(\frac{\Delta\tau}{V}\right)^2 = W^2$$

Similarly, we can find

$$W_2 = \frac{\Delta\tau}{V}\left(1 - \frac{\Delta\tau}{V}\right) = W(1 - W)$$

$$W_3 = \frac{\Delta\tau}{V}\left(1 - \frac{\Delta\tau}{V}\right) = W(1 - W)$$

$$W_4 = \left(1 - \frac{\Delta\tau}{V}\right)^2 = (1 - W)^2$$

We are interested in the probability of $\Delta\tau$ containing n molecules, i.e. in the given case 2, 1, or 0. It is not difficult to see that

$$W(2) = W_1 = W^2$$

since only when the event *1* happens are both molecules in $\Delta\tau$. Further,

$$W(1) = W_2 + W_3 = 2W(1 - W)$$

since in the second and the third case one molecule is in $\Delta\tau$. Finally,

$$W(0) = W_4 = (1 - W)^2$$

If the number of molecules is three and they are designated *1*, *2*, and *3*, the events listed in Table 1.1 are possible. This table gives the values of the probabilities W_i corresponding to the different possible distributions of the molecules, and also of the required probabilities $W(3)$, $W(2)$, $W(1)$, and $W(0)$.

Going over now to the general case of N molecules, we can show that

$$W(n) = \frac{N!}{n!\,(N-n)!}\, W^n\,(1-W)^{N-n} \qquad (1.4)$$

Table 1.1

Number of event	Molecules in $\Delta\tau$	Molecules in $V - \Delta\tau$	Number of molecules in $\Delta\tau$	Probabilities of events W_i	Probabilities $W(n)$
1	1, 2, 3	—	3	W^3	$W(3) = W^3$
2	1, 2	3			
3	1, 3	2	2	$W^2(1-W)$	$W(2) = 3\,W^2\,(1-W)$
4	2, 3	1			
5	1	2, 3			
6	2	1, 3	1	$W(1-W)^2$	$W(1) = 3W\,(1-W)^2$
7	3	1, 2			
8	—	1, 2, 3	0	$(1-W)^3$	$W(0) = (1-W)^3$

Indeed, the probability of the fact that n definite molecules will be in the volume $\Delta\tau$, and the remaining $N - n$ molecules outside it is

$$W^n (1 - W)^{N-n} \tag{1.5}$$

The number of similar events differing from one another in what n molecules of their total number N are in $\Delta\tau$ equals the number of combinations of N taken n at a time, i.e.

$$\frac{N!}{n! (N - n)!} \tag{1.6}$$

Hence, summation of the probabilities of all the events in which n molecules were in $\Delta\tau$, i.e. multiplication of (1.5) by (1.6), leads to the general formula (1.4).

Events in which the number of molecules getting into $\Delta\tau$ is 0, 1, 2, 3, . . ., are mutually exclusive and form a complete set. The sum of the probabilities of these events must equal unity. It is quite simple to convince ourselves that this is indeed correct:

$$\sum_{n=0}^{N} W(n) = \sum_{n=0}^{N} \frac{N!}{n! (N-n)!} W^n (1 - W)^{N-n}$$

Using the binomial theorem, we can write

$$\sum_{n=0}^{N} \frac{N!}{n! (N-n)!} W^n (1 - W)^{N-n} = [W + (1 - W)]^N = 1^N = 1$$

The relationship of the probabilities $W(n)$ to the binomial formula is why the dependence of $W(n)$ on the number of molecules n was given the name of the **binomial distribution of probabilities**.

Let us consider as an example the distribution of *six* molecules in a vessel mentally divided into *two* equal parts, i.e. when $\Delta\tau = V/2$. Having calculated the binomial coefficients, we can obtain the results depicted graphically in Fig. 1.6, where the dots indicate the corresponding values of the probabilities. It can be seen that the event having the greatest probability consists in the number n being equal to three, i.e. half of the vessel will contain half of the total number of molecules. The absence of molecules ($n = 0$) or all of them getting together in one half of the

vessel ($n = 6$) are considerably less probable and are there-fore observed much less frequently (20 times less frequently).

The binomial distribution is used in solving a multitude of problems, and not only in the example considered above. Indeed, assume that we know the probability of a molecule having a definite feature (for instance, a velocity ranging
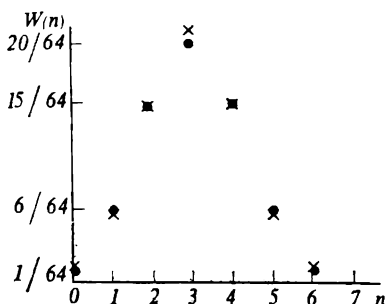
Fig. 1.6

from 100 to 150 m/s, or that it has travelled without col-lisions with other molecules a path exceeding 1 mm, and so on). What is the probability of n molecules among the total number of N having this same feature? If the corresponding events for different molecules are independent and their probability is W, the answer is given by the binomial dis-tribution (1.4). To convince ourselves in the truth of this conclusion, it is sufficient to take into account that the specific content of the problem given above was used only in finding the value of the probability $W = \Delta \tau / V$ of having a definite feature (the getting of a molecule into $\Delta \tau$ at the instant t). All the remaining reasoning does not depend on what feature specifically we have in mind.

1.6. Stirling's Formula

In solving statistical problems, we have to do with a tre-mendous number of molecules. Consequently, the use of a number of formulas, particularly the binomial distribu-tion, is not convenient because factorials of very large num-bers are encountered. For example, at standard temperature

and pressure, one cubic centimetre of a gas contains 2.69×10^{19} molecules. If we want to determine the probability of 10^{16} of them being in a volume of $\Delta \tau = 1 \; mm^3$, the use of formula (1.4) requires that we compute $10^{16}!$ and $2.69 \times 10^{19}!$. If we take into consideration that difficulties are already encountered in computing $30!$ or $40!$, it is quite obvious that it is desirable to have a formula allowing us
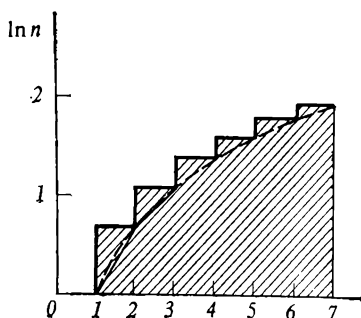
Fig. 1.7

to rapidly assess the values of factorials of large numbers. The corresponding expression was obtained by J. Stirling and bears his name.

It is convenient to begin with a consideration not of $N!$, but of the natural logarithm of this expression

$$\ln N! = \ln 1 + \ln 2 + \ln 3 + \ldots + \ln N = \sum_{n=1}^{N} \ln n$$

The values of $\ln n$ have been plotted in Fig. 1.7. The sum we are interested in is the hatched area confined by the stepped line and the axis of abscissas. Indeed, the area of each step equals its width, i.e. unity, multiplied by its height, namely, by $\ln n$, and therefore equals $\ln n$. The area of the entire figure equals the sum of the areas of the steps from the first one having a zero area ($\ln 1 = 0$) to the last one ($\ln N$): $S = \sum_{n=1}^{N} \ln n$. To assess the area S, let us plot in the graph a curve given by the equation $y = \ln x$, where x is the continuous coordinate of the axis of abscissas. This line is dashed in Fig. 1.7. It is quite simple to evaluate the

area S' under the dashed line and confined at the right by the ordinate erected at $x = N$:

$$S' = \int\limits_{1}^{N} \ln x \, dx = x \ln x \big|_1^N - \int\limits_{1}^{N} x \frac{1}{x} \, dx = N \ln N - (N-1) \quad (1.7)$$

Formula (1.7) gives an approximate assessment of the area S if we assume that $S \approx S'$, but S can be determined more accurately. Inspection of the graph shows that $S' < S$, and a much better approximation is obtained if we add to S' the area of the triangles shown in Fig. 1.7. The area of one triangle, whose base is 1 and whose altitude is the difference of $\ln (n + 1)$ and $\ln n$, is given by the expression

$$\frac{1}{2} [\ln (n+1) - \ln n]$$

Summation of the areas of all the triangles yields

$$\frac{1}{2} \ln 2 + \frac{1}{2} [\ln 3 - \ln 2] + \frac{1}{2} [\ln 4 - \ln 3] + \ldots$$

$$\ldots + \frac{1}{2} [\ln N - \ln (N-1)] = \frac{1}{2} \ln N$$

We can thus approximately write that

$$S \approx N \ln N - N + \frac{1}{2} \ln N + 1$$

or, since $N! = e^S$,

$$N! = \exp \left(N \ln N - N + \frac{1}{2} \ln N + 1 \right) = e N^N e^{-N} \sqrt{N}$$

The strict derivation given in courses of analysis shows that a more accurate result has the form

$$N! = \sqrt{2\pi} \, N^N e^{-N} \sqrt{N} \qquad (1.8)$$

i.e. there is a slight difference in the value of the constant factor ($e = 2.718 \ldots$, $\sqrt{2\pi} = 2.506 \ldots$).

The relative error of formula (1.8) diminishes with increasing N. We shall give two examples. When $N = 4$, the exact value of 4! is 24, while Stirling's formula gives

$$\sqrt{2\pi} \sqrt{4} \times 4^4 e^{-4} \approx 23.7$$

3*

When $N = 6$, the exact value of $N!$ is 720, while by formula (1.8) we obtain 716. In the first example, the relative error is 1.25%, and in the second, 0.56%. The relative error rapidly diminishes with increasing values of N.

Chapter 2

RANDOM VARIABLES
AND THEIR CHARACTERISTICS

2.1. Random Variable

In the applications of the theory of probability to questions of statistical physics, we have to do with the notion of a **random variable.** *A variable that can take on various numerical values with a definite probability is said to be random.* We actually encountered this concept in the preceding chapter. Indeed, the number of molecules in the volume element $\Delta\tau$ selected in a vessel of the volume V is the corresponding example, because this number takes on the values 0, 1, 2, . . ., N, and each of them is realized with a definite probability $W(n)$ determined by formula (1.4) of the binomial distribution. The number of molecules in the volume element $\Delta\tau$ is thus a random variable. Such a random variable is said to be **discrete** because it takes on values differing from one another by a finite value (in the given example, integral values 0, 1, 2, . . ., N).

Continuous random variables are also encountered. They take on a continuous series of values. Probably, the simplest example of a continuous random variable is the coordinate of the molecule A in the vessel V. Let us place the origin of coordinates in one of the corners of a rectangular vessel as shown in Fig. 2.1. Now, the coordinate of the molecule z_A along the z-axis can take on any values within the interval from $z = 0$ to $z = a$, where a is the dimension of the vessel in the direction of the z-axis.

It is not correct to be interested in the probability of a continuous random variable having a given value. The correct statement of the problem consists in establishing the probability of a random variable taking on a value ranging

from z to $z + dz$. If the interval dz is infinitely small, the corresponding probability dW is also infinitely small, and, consequently, it must be proportional to the interval dz. We can write the following expression for the required probability:

$$dW = w(z) \, dz \qquad (2.1)$$

where $w(z)$ is a function known as the **probability density**. Its dimension is inversely proportional to that of the random
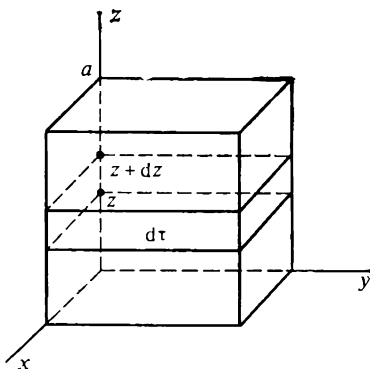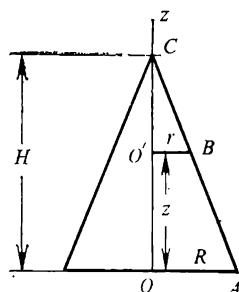
Fig. 2.1   Fig. 2.2

variable z because the probability dW is a dimensionless quantity. Hence, *the probability density for a random variable whose values are designated by z is the function w (z) which, when multiplied by* dz, *gives the probability of the value of the random variable being within the interval from z to z* $+$ *dz.* If the interval dz equals zero, the corresponding probability is also zero, therefore there is no sense in being interested in the probability of a separate value of a continuous random variable.

To explain the concept we have introduced, let us turn to the example in which the coordinate z of the molecule A is a continuous random variable. We have to find the probability density for this random variable. The molecule's coordinate gets into the interval dz if, as can be seen from Fig. 2.1, the molecule itself is within the volume $d\tau$ confined by two planes drawn through the points z and $z + dz$ at

right angles to the z-axis. Let the area of the base of the vessel be S, hence its volume is $d\tau = S\,dz$. Since the volume of the entire vessel $V = aS$, we obtain the following expression for the probability:

$$dW = \frac{d\tau}{V} = \frac{S\,dz}{aS} = \frac{1}{a}\,dz$$

Inspection of the last equation shows that the probability density for the molecule's coordinate is

$$w(z) = \frac{1}{a}$$

As should be expected, the dimension of the probability density is the reciprocal of the length because the random variable z itself has the dimension of length.

That the probability density was found to be a constant quantity is associated with the specific features of the given problem in which the vessel is rectangular and all the positions of the molecule A in the vessel are considered to be equally possible. If the vessel were placed in the field of action of external forces (for example, if we took into account the action of the force of gravity), or if it had a shape other than rectangular, the probability density would not be a constant quantity.

For instance for a conical vessel (Fig. 2.2), disregarding the action of the force of gravity, we can find the following expression for the probability dW:

$$dW = \frac{d\tau}{V} = \frac{\pi r^2\,dz}{(1/3)\,\pi R^2 H}$$

where r is the radius of a circular cone section at the altitude z from the base and, consequently, $\pi r^2\,dz$ is the volume of the cone layer confined between the planes passing at right angles to its axis at a distance of z and $z + dz$ from the base, R is the radius of the base, and H is the altitude of the cone. Since from the similarity of the triangles COA and $CO'B$ it follows that $\frac{r}{R} = \frac{H-z}{H}$, we have

$$r^2 = \frac{(H-z)^2}{H^2}\,R^2$$

If we also take into account that the volume of the cone is $V = (1/3)\,\pi R^2 H$, we have

$$dW = 3\,\frac{(H-z)^2}{H^3}\,dz$$

i.e. the probability density is

$$w(z) = 3\,\frac{(H-z)^2}{H^3}$$

We often have to do with random vector variables, i.e. with vectors having a various length and direction which
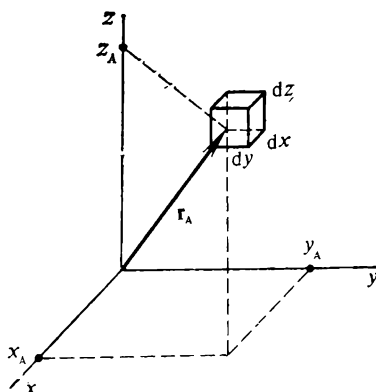
Fig. 2.3

they take on with a definite probability. A very simple example of a random vector variable is the position vector of the molecule A placed in a vessel of the volume V. Let us introduce a Cartesian system of coordinates along whose axes we shall lay off the components x_A, y_A, and z_A of the random vector $\mathbf{r}_A$ and plot near the points x, y, and z the infinitely small rectangular volume $d\tau = dx\,dy\,dz$ (Fig. 2.3). What is the probability of the tip of the vector $\mathbf{r}_A$ being within the earmarked volume $d\tau$? Since the volume is infinitely small, the probability dW must be proportional to it, i.e.

$$dW = w(x,\,y,\,z)\,d\tau \tag{2.2}$$

The quantity w, generally speaking, which depends on the coordinates x, y, and z, is called the probability density

of the random vector variable **r**. Hence, *the product of the probability density w of a random vector variable and a volume element* dτ *gives the probability of the fact that the tip of the vector* **r** *is inside* dτ *or, in other words, that the following conditions are simultaneously observed: the x-, y-, and z-components of* **r** *are contained within the intervals from x to x + dx, from y to y + dy, and from z to z + dz, respectively.*

In the example being considered, the probability density w is the reciprocal of the volume of the vessel. Indeed, back in Sec. 1.2, we established that the probability of the molecule A getting into the volume element dτ, i.e. the probability of the fact that the tip of its position vector will be in this element, is

$$dW = \frac{d\tau}{V}$$

Comparing this equation with Eq. (2.2), we can conclude that

$$w = \frac{1}{V} \qquad (2.3)$$

If the components of a random vector are independent, in this important particular case the probability density $w\,(x,\,y,\,z)$ is represented as the product of three probability densities

$$w\,(x,\,y,\,z)\,d\tau = w_x\,(x)\,dx \cdot w_y\,(y)\,dy \cdot w_z\,(z)\,dz \qquad (2.4)$$

so that the probability of the component x getting into the interval dx equals $w_x\,(x)\,dx$ and does not depend on what values the other components acquire.

Formula (2.4) has a simple probabilistic meaning and signifies that the probability of the vector **r** getting into dτ equals the product of the probabilities of three independent events, namely of the probability that the component x will get into the interval dx, that the component y will get into the interval dy, and that the component z will get into the interval dz. The formula (2.3) obtained above illustrates this case. Since the volume of a vessel having the shape of a rectangular parallelepiped equals the product of its sides, we have

$$V = cba$$

where c, b, and a are the lengths of the sides along the x-, y-, and z-axes, respectively. Using this relation, we can

write the following expression for the probability density:

$$w = \frac{1}{V} = \frac{1}{c} \times \frac{1}{b} \times \frac{1}{a}$$

whence

$$w_x = \frac{1}{c}; \quad w_y = \frac{1}{b}; \quad w_z = \frac{1}{a}$$

2.2. Mean Value

A knowledge of the probabilities of separate values of a discrete random variable or of the probability density for a continuous random variable allows us to find its mean value, or, as is said in other words, its **mathematical expectation**. We shall obtain the general rule by considering the following specific example. Assume that the volume $\Delta\tau$ is separated in the vessel V, and the random variable we are interested in is the number of molecules in $\Delta\tau$ at a certain instant t. Assume further that we have run a great number of trials M in each of which we registered the number of molecules in $\Delta\tau$. Assume that m_1 times we registered the value n_1, m_2 times—the value n_2, and so on. Hence, we find the mean value of the number of molecules in $\Delta\tau$ by the formula

$$\langle n \rangle = \frac{m_1 n_1 + m_2 n_2 + \ldots}{m_1 + m_2 + \ldots} = \frac{m_1 n_1 + m_2 n_2 + \ldots}{M}$$

$$= \frac{m_1}{M} n_1 + \frac{m_2}{M} n_2 + \ldots$$

If the number of trials is sufficiently great, the ratios m_1/M, m_2/M, etc. become equal to the probabilities of the relevant values of n, i.e.

$$\langle n \rangle = w(n_1) n_1 + w(n_2) n_2 + \ldots = \sum_i w(n_i) n_i \qquad (2.5)$$

where the sum is evaluated over all possible values of the random variable n_i ($n_i = 0, 1, \ldots, N$; here N is the number of molecules in the vessel).

When we are considering a continuous random variable z, since the probability of its value being in the interval dz is $w(z)\,dz$, we must summate the expression $zw(z)\,dz$ over all the values of z, i.e. over all the intervals dz to find the mean value. This signifies that the **rule for determining**

the mean value of a continuous random variable can be written as follows:

$$\langle z \rangle = \int z w(z) \, dz \tag{2.6}$$

where the integral (sum) is evaluated over all possible values of the random variable.

Let us return to the mean number of particles in the volume $\Delta\tau$. Assume that the total number of particles in a vessel of the volume V is N. The mean value is determined by formula (2.5) in which by $w(n_i)$ we must understand the probability of n_i particles being in $\Delta\tau$, i.e. expression (1.4). Hence,

$$\langle n \rangle = \sum_{n_i=0}^{N} n_i \, \frac{N!}{n_i!\,(N-n_i)!} \left(\frac{\Delta\tau}{V} \right)^{n_i} \left(1 - \frac{\Delta\tau}{V} \right)^{N-n_i}$$

In evaluating the above sum, we must give attention to the fact that actually summation is conducted from $n_i = 1$ because the addend with $n_i = 0$ vanishes (it must be taken into account that $0! = 1$). In this connection, cancelling n_i, we can write

$$\langle n \rangle = \sum_{n_i=1}^{N} \frac{N!}{(n_i-1)!\,(N-n_i)!} \left(\frac{\Delta\tau}{V} \right)^{n_i} \left(1 - \frac{\Delta\tau}{V} \right)^{N-n_i}$$

If we designate $n_i - 1$ by k, where k takes on the values $0, 1, \ldots, N - 1$, the expression for $\langle n \rangle$ can be written as

$$\langle n \rangle = \sum_{k=0}^{N-1} \frac{N!}{k!\,(N-1-k)!} \, \frac{\Delta\tau}{V} \left(\frac{\Delta\tau}{V} \right)^{k} \left(1 - \frac{\Delta\tau}{V} \right)^{N-1-k}$$

We remove the common factor from inside the sum, and therefore obtain

$$\langle n \rangle = N \, \frac{\Delta\tau}{V} \sum_{k=0}^{N-1} \frac{(N-1)!}{k!\,(N-1-k)!} \left(\frac{\Delta\tau}{V} \right)^{k} \left(1 - \frac{\Delta\tau}{V} \right)^{N-1-k}$$

By the formula of the binomial theorem in complete accordance with what occurred in similar calculations in Sec. 1.5,

we have

$$\sum_{k=0}^{N-1} \frac{(N-1)!}{k!\,(N-1-k)!} \left(\frac{\Delta\tau}{V}\right)^k \left(1-\frac{\Delta\tau}{V}\right)^{N-1-k}$$

$$=\left[\frac{\Delta\tau}{V}+\left(1-\frac{\Delta\tau}{V}\right)\right]^{N-1}=1$$

Hence,

$$\langle n\rangle = N\,\frac{\Delta\tau}{V} \tag{2.7}$$

i.e. the mean number of particles in the volume $\Delta\tau$ equals the total number of particles N in the vessel multiplied by the probability $(\Delta\tau/V)$ of the particle getting into $\Delta\tau$.

We shall calculate the mean value of a continuous random variable using the example of the z-coordinate of a molecule in a rectangular vessel. We have shown on an earlier page that the probability density in this case is $w(z) = 1/a$. The mean value of z is calculated by (2.6):

$$\langle z\rangle = \int_0^a z\,\frac{1}{a}\,\mathrm{d}z = \frac{1}{a}\,\frac{z^2}{2}\,\Big|_0^a = \frac{a}{2} \tag{2.8}$$

i.e. we have obtained a result that was intuitively obvious from the very beginning.

It is often important in applications to know the mean value of the function of a random variable, for example, of the square (or another power) of the number of particles in the volume $\Delta\tau$ or of the square of the coordinate of a molecule z^2. Applying the above reasoning not to the random variable n_i itself, but to a function $\psi(n_i)$ of it, we can readily show that the mean value should be determined by the formula

$$\langle \psi(n_i)\rangle = \sum_i \psi(n_i)\,w(n_i) \tag{2.9}$$

The mean value of the function of a continuous random variable is evaluated with the aid of a rule whose meaning is similar:

$$\langle \psi(z)\rangle = \int \psi(z)\,w(z)\,\mathrm{d}z \tag{2.10}$$

The integral is evaluated over all possible values of the random variable z.

Hence, *the mean value (mathematical expectation) of the function of a random variable is evaluated as the sum of the products of this function and the probability of the value of its argument*, i.e. by formula (2.9) for a discrete random variable and by formula (2.10) for a continuous one.

Let us use the above rule for calculating a very important characteristic known as a **dispersion**. *A dispersion is the mathematical expectation of the square of the deviation of a random variable from its mean value*, i.e.

$$D\left(n_i\right) = \langle(n_i - \langle n_i \rangle)^2\rangle, \quad D\left(z\right) = \langle(z - \langle z \rangle)^2\rangle \qquad (2.11)$$

The importance of this characteristic follows from the fact that it determines the degree of scattering of a random variable, i.e. in a certain meaning the dispersion is a measure of randomness or chance. If a non-random variable is considered as a random one taking on the same value with a probability of unity, it is clear that its deviation from the mean value is zero, and, consequently, the dispersion is also zero. Hence, the dispersion of a non-random variable is zero, while for a random variable it is the greater, the wider is the scattering of its values.

Formulas (2.11) can be written in a more convenient form for calculations. It is obtained below only for an example of a continuous random variable because in the discrete case all we have to do is to substitute summation for integration.

In accordance with the definition of a dispersion,

$$D\left(z\right) = \int \left(z - \langle z \rangle\right)^2 w\left(z\right) \mathrm{d}z = \int \left(z^2 - 2z \langle z \rangle + \langle z \rangle^2\right) w\left(z\right) \mathrm{d}z$$

$$= \int z^2 w\left(z\right) \mathrm{d}z - \int 2z \langle z \rangle w\left(z\right) \mathrm{d}z + \int \langle z \rangle^2 w\left(z\right) \mathrm{d}z$$

Since $\langle z \rangle^2$ is simply a number, the last integral equals

$$\int \langle z \rangle^2 w\left(z\right) \mathrm{d}z = \langle z \rangle^2 \int w\left(z\right) \mathrm{d}z$$

The **normalization condition** for the probability density of a random variable is

$$\int w\left(z\right) \mathrm{d}z = 1$$

It follows from the fact that the values taken on by the random variable from different intervals dz form a complete

set of mutually exclusive events. The condition of normalization signifies that the random variable with a probability of unity will take on any of the possible values.

The next-to-last integral in the expression for the dispersion is transformed as follows:

$$\int 2z \langle z \rangle w(z) \, dz = 2 \langle z \rangle \int zw(z) \, dz = 2 \langle z \rangle \langle z \rangle = 2 \langle z \rangle^2$$

Since the first integral has the meaning of the mean value of the square of the random variable and must be designated by $\langle z^2 \rangle$, the final result with account taken of the normalization condition is written as

$$D(z) = \langle z^2 \rangle - 2 \langle z \rangle^2 + \langle z \rangle^2 = \langle z^2 \rangle - \langle z \rangle^2 \qquad (2.12)$$

A similar formula also holds for a discrete random variable:

$$D(n_i) = \langle n_i^2 \rangle - \langle n_i \rangle^2$$

Using the example of a dispersion, we can readily show that the mean value of a function of a random variable does not equal the value of this function when the mean value of the random variable itself is taken as its argument. Indeed, in the given case, we have to evaluate the mean value of the function $f(z) = z^2$. Its mean value is $\langle z^2 \rangle$ (the mean value sign relates to the entire function), and it does not equal the square of the mean value $\langle z \rangle^2$. If such equality were to occur, the dispersion would vanish. We shall show that this is not what happens, using the example already treated in the present section.

Let us calculate the **dispersion of the coordinate** of a molecule in a rectangular vessel. To use (2.12), we calculate $\langle z^2 \rangle$:

$$\langle z^2 \rangle = \int\limits_0^a z^2 \frac{1}{a} \, dz = \frac{a^2}{3}$$

Since $\langle z \rangle = a/2$, by (2.12) we have

$$D(z) = \frac{a^2}{3} - \frac{a^2}{4} = \frac{a^2}{12}$$

The following **properties of mean values and a dispersion** are very important for their applications.

(a) If we summate two functions $f_1(x, y, z)$ and

$f_2(x, y, z)$, where $\mathbf{r} = \{x, y, z\}$ is a random vector, *the mean value of the sum of the functions equals the sum of their mean values.*

Indeed, when $\mathbf{r}$ is a continuous random vector, we have

$$\langle [f_1(x, y, z) + f_2(x, y, z)] \rangle = \int (f_1 + f_2) w(x, y, z) \, d\tau$$

$$= \int f_1 w(x, y, z) \, d\tau + \int f_2 w(x, y, z) \, d\tau = \langle f_1 \rangle + \langle f_2 \rangle$$

This property is proved in a similar way for discrete random variables.

(b) If a function of a random vector $\mathbf{r}$ is multiplied by a constant number a, the mean value of the product equals the mean value of f_1 multiplied by a. In other words, this property is formulated as follows: *a constant factor may be removed from the mean value sign.* The proof is conducted as follows:

$$\langle af_1 \rangle = \int af_1 w \, d\tau = a \int f_1 w \, d\tau = a \langle f_1 \rangle$$

(the proof is similar for a discrete random variable).

(c) If there are several (for example, three) functions $f_1(x)$, $f_2(y)$, and $f_3(z)$ of the components x, y, and z of the random vector $\mathbf{r} = \{x, y, z\}$, and *if the random variables x, y, and z are independent*, so that

$$w(x, y, z) \, d\tau = w_x(x) \, dx \cdot w_y(y) \, dy \cdot w_z(z) \, dz$$

the mean value of the product $f_1(x) \cdot f_2(y) \cdot f_3(z)$ equals the product of their mean values.

Indeed,

$$\langle f_1 \cdot f_2 \cdot f_3 \rangle = \int \int \int f_1(x) f_2(y) f_3(z) w_x(x) w_y(y) w_z(z) \, dx \, dy \, dz$$

$$= \int f_1(x) w_x(x) \, dx \cdot \int f_2(y) w_y(y) \, dy \cdot \int f_3(z) w_z(z) \, dz$$

$$= \langle f_1 \rangle \cdot \langle f_2 \rangle \cdot \langle f_3 \rangle$$

(d) *The dispersion of the sum of several independent random variables equals the sum of their dispersions.*

Let x, y, and z be independent random variables; hence, by definition, we have

$$D(x + y + z) = \langle (x + y + z)^2 \rangle - \langle (x + y + z) \rangle^2$$

Let us square the first parentheses and use the property (a) in the second ones:

$$D\ (x + y + z) = \langle(x^2 + y^2 + z^2 + 2xy + 2xz + 2yz)\rangle$$
$$- (\langle x \rangle + \langle y \rangle + \langle z \rangle)^2$$

Let us square the second parentheses and apply the property (a) to the first ones:

$$D\ (x + y + z) = (\langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle + \langle 2xy \rangle + \langle 2xz \rangle$$
$$+ \langle 2yz \rangle - \langle x \rangle^2 - \langle y \rangle^2 - \langle z \rangle^2$$
$$- 2 \langle x \rangle \langle y \rangle - 2 \langle x \rangle \langle z \rangle - 2 \langle y \rangle \langle z \rangle)$$

With a view to the property (b), we remove the factor 2 from the mean value sign so that, for instance, $\langle 2xy \rangle = 2 \langle xy \rangle$. Moreover, since the quantities x, y, and z are independent, according to the property (c) we have

$$\langle xy \rangle = \langle x \rangle \langle y \rangle, \quad \langle xz \rangle = \langle x \rangle \langle z \rangle, \quad \langle yz \rangle = \langle y \rangle \langle z \rangle$$

and we now see that all the terms containing products of the mean values of different random variables cancel one another. Consequently,

$$D\ (x + y + z) = \langle x^2 \rangle - \langle x \rangle^2 + \langle y^2 \rangle - \langle y \rangle^2 + \langle z^2 \rangle$$
$$- \langle z \rangle^2 = D\ (x) + D\ (y) + D\ (z)$$

Q.E.D.

The above properties quite often allow us to simplify the calculation of mean values and a dispersion. Let us again consider as an example the number of particles in the volume $\Delta\tau$. If we associate with each molecule the random variable n_A taking on the value 1 when the molecule is in $\Delta\tau$ and 0 when it is outside this volume, the number of particles in $\Delta\tau$ can be considered as the sum of these random variables for all the molecules of the gas. With a view to the property (a), the mean value of the number of particles equals the sum of the mathematical expectations n_A. The latter quantity is calculated by the general formula

$$\langle n_A \rangle = 1 \times \frac{\Delta\tau}{V} + 0 \times \left(1 - \frac{\Delta\tau}{V}\right) = \frac{\Delta\tau}{V}$$

Since the mathematical expectation for all the molecules is the same, their sum is evaluated by multiplying the expression obtained by the total number of molecules N. Conse-

quently,

$$\langle n \rangle = N \frac{\Delta \tau}{V}$$

The dispersion of the number of particles in $\Delta \tau$ is evaluated just as simply. It is first necessary to find $\langle n_A^2 \rangle$:

$$\langle n_A^2 \rangle = 1^2 \times \frac{\Delta \tau}{V} + 0^2 \times \left(1 - \frac{\Delta \tau}{V} \right) = \frac{\Delta \tau}{V}$$

and then the dispersion of this quantity:

$$D_{nA} = \langle n_A^2 \rangle - \langle n_A \rangle^2 = \frac{\Delta \tau}{V} - \left(\frac{\Delta \tau}{V} \right)^2 = \frac{\Delta \tau}{V} \left(1 - \frac{\Delta \tau}{V} \right)$$

The dispersion of the total number of particles in $\Delta \tau$ is determined with the aid of the property (d). It equals

$$D = N D_{nA} = N \frac{\Delta \tau}{V} \left(1 - \frac{\Delta \tau}{V} \right) \qquad (2.13)$$

The direct calculation of this quantity is considerably more cumbersome.

2.3. Poisson Distribution

In Chapter 1, we mentioned that the use of the binomial distribution to calculate probabilities at large values of the total number of molecules N is not convenient, and we obtained Stirling's formula facilitating the evaluation of factorials of large numbers. By using Stirling's formula, we can simplify the binomial distribution and reduce it to other ones that are more convenient for calculations.

In the present section, we treat the case when at a large value of the number N, the small values of the number of molecules n in the volume $\Delta \tau$ are of the main interest, i.e. we assume that the large values of n have such a low probability that they may be ignored. Assume, for example, that a vessel contains N molecules, where N is of the order of 10^{19}. Let us separate the volume $\Delta \tau$ that is so small in comparison with the total volume V of the vessel that we may encounter $n = 0$, 1, 2, or 3 molecules in it, and the probability that the number of molecules will exceed, say, $n = 10$ is very low. For this purpose, the volume must be such that the mean number of molecules in it, equal by (2.7) to $\langle n \rangle = N (\Delta \tau / V)$ will be much smaller than the limiting

number $n = 10$ we have chosen, for instance, $\langle n \rangle = 3$. Naturally, the number 3 has been chosen arbitrarily and with the same success could be replaced by any other number that is sufficiently small in comparison with the total number of molecules N; however, at relatively great values of $\langle n \rangle$, it is more convenient to use a different approximation of the binomial distribution that will be given in the following section and that is knowingly unsuitable at low values of $\langle n \rangle$ (at $\langle n \rangle \leqslant 3$).

The exact value of the probability by the formula of the binomial distribution (1.4) is

$$W(n) = \frac{N!}{n!\,(N-n)!} \left(\frac{\Delta\tau}{V} \right)^n \left(1 - \frac{\Delta\tau}{V} \right)^{N-n}$$

Taking advantage of the fact that N and $N - n$ are very large numbers, we replace their factorials with the aid of Stirling's formula

$$W(n) = \frac{N^N e^{-N} N^{1/2} \sqrt{2\pi}}{n!\,(N-n)^{N-n}\,e^{-N+n}\,(N-n)^{1/2}\,\sqrt{2\pi}}$$
$$\times \left(\frac{\Delta\tau}{V} \right)^n \left(1 - \frac{\Delta\tau}{V} \right)^{N-n}$$

Dividing both the numerator and denominator by $\sqrt{2\pi} \times N^{N-n} N^{1/2} e^{-N}$, we obtain

$$W(n) = \frac{N^n\,(\Delta\tau/V)^n\,(1 - \Delta\tau/V)^{N-n}}{n!\,(1 - n/N)^{N-n}\,e^n\,(1 - n/N)^{1/2}} \qquad (2.14)$$

The factor in the denominator, i.e.

$$(1 - n/N)^{N-n} = \frac{(1 - n/N)^N}{(1 - n/N)^n}$$

is transformed as follows. It is known from analysis that the expression $(1 - n/N)^N$ at $N \to \infty$ (i.e. in practice at sufficiently large N's) equals e^{-n}. The expression $(1 - n/N)^n$, since n/N is a very small quantity, is close to unity. Indeed, if $n \ll \sqrt{N}$, for example, $n = 0.3\sqrt{N}$, we have

$$\left(1 - \frac{n}{N} \right)^n = \left(1 - \frac{0.3}{\sqrt{N}} \right)^{0.3\sqrt{N}}$$

$$= \left[\left(1 - \frac{0.3}{\sqrt{N}} \right)^{\sqrt{N}} \right]^{0.3} = (e^{-0.3})^{0.3} = e^{-0.09} = 0.91$$

Hence,

$$\left(1 - \frac{n}{N}\right)^{N-n} \approx e^{-n}$$

Naturally, with the assumptions we have made, another factor from the denominator of (2.14) also approximately equals unity:

$$\left(1 - \frac{n}{N}\right)^{1/2} \approx 1$$

To complete our calculations, it remains for us to consider the expression encountered in the numerator of (2.14):

$$\left(1 - \frac{\Delta\tau}{V}\right)^{N-n} = \frac{\left(1 - \frac{N(\Delta\tau/V)}{N}\right)^{N}}{(1 - \Delta\tau/V)^{n}} \qquad (2.15)$$

If $n\Delta\tau \ll V$, by analogy with the preceding material, the denominator in (2.15) equals unity. The quantity $N(\Delta\tau/V)$ equal to the mean value of the number of molecules in $\Delta\tau$, which we shall designate by $\langle n \rangle$, is much smaller than N by assumption, and therefore

$$\left(1 - \frac{\langle n \rangle}{N}\right)^{N} = e^{-\langle n \rangle}$$

For the probability we are interested in, the following expression has thus been found to hold:

$$W(n) = \frac{[N(\Delta\tau/V)]^{n} e^{-\langle n \rangle}}{n! e^{-n} e^{n}} = \frac{\langle n \rangle^{n} e^{-\langle n \rangle}}{n!} \qquad (2.16)$$

Formula (2.16) is known as the **Poisson distribution**. It determines the probability of $\Delta\tau$ containing n molecules (at a mean value of the number of molecules in $\Delta\tau$ equal to $\langle n \rangle$) and is correct if the total number of molecules in the vessel is much greater than $\langle n \rangle^2$.

Since the Poisson distribution is the limiting case of a binomial one when $\langle n \rangle^2 \ll N$, or, in other words, when $\langle n \rangle / N = \Delta\tau/V \to 0$, the dispersion of a random variable observing the Poisson distribution is obtained from (2.13) by the same limiting process, i.e. is found to equal the mean value of the number n:

$$D = \langle n \rangle \qquad (2.17)$$

2.4. Gaussian Distribution

Another useful approximation can be used when not only the total number of molecules N is large, but also the number of molecules n in the volume element $\Delta\tau$, as well as the number of molecules $N - n$ remaining outside this volume. This case is realized very often in practice because for it to occur it is sufficient that the mean number of molecules in the element $\Delta\tau$

$$\langle n \rangle = \frac{N\Delta\tau}{V} \tag{2.18}$$

be large, but not too close to the total number, in other words, the volume $\Delta\tau$ must not be too small in comparison with V, and not too close to the entire volume. We shall see from the following that the Gaussian distribution is already sufficiently accurate if $\langle n \rangle$ and $N - \langle n \rangle$ are greater than 3, and its accuracy grows with $\langle n \rangle$ and $N - \langle n \rangle$.

The probability of the volume $\Delta\tau$ containing n particles provided that the mean number of particles $\langle n \rangle$ in $\Delta\tau$ and the mean number of particles $N - \langle n \rangle$ outside this volume are sufficiently large is given by a formula known as the **Gaussian distribution** having the following form:

$$W(n) = \frac{1}{\sqrt{2\pi D}} \exp\left[-\frac{(n-\langle n \rangle)^2}{2D} \right] \tag{2.19}$$

The Gaussian distribution (2.19) is used most frequently when the number of molecules in $\Delta\tau$ is very large. In practice, we virtually never have to know the probability of there being exactly n molecules in $\Delta\tau$; we are usually interested in the probability δW of the fact that the number of molecules is confined within the interval of values from n to $n + \delta n$. If the quantity δn is sufficiently small (much smaller than $\sqrt{D}$), the probability $W(n)$ calculated by (2.19) for any n of the interval δn is virtually the same. In this connection, the probability δW is obtained by multiplying the probability $W(n)$ taken for any (it does not matter which one) value of n from the interval being considered and the magnitude of the interval δn, i.e.

$$\delta W = \frac{1}{\sqrt{2\pi D}} \exp\left[-\frac{(n-\langle n \rangle)^2}{2D} \right] \delta n \tag{2.20}$$

Formula (2.20) shows that with a large number of molecules the variable n may be considered a continuous random variable, and the probability of its values being between n and $n + \delta n$ is determined by formula (2.20), i.e. the relevant probability density is

$$w(n) = \frac{1}{\sqrt{2\pi D}} \exp\left[-\frac{(n-\langle n \rangle)^2}{2D} \right]$$

If it is necessary to determine the probability W of the fact that n is contained in the interval from n_1 to n_2 and the interval is not assumed to be small in comparison with $\sqrt{D}$, it is necessary to take into account the change in the probability density in this interval and take advantage of the conventional rule for continuous random variables:

$$W = \int_{n_1}^{n_2} w(n)\, dn = \int_{n_1}^{n_2} \frac{1}{\sqrt{2\pi D}} \exp\left[-\frac{(n-\langle n \rangle)^2}{2D} \right] dn$$

In exactly the same way when determining the mean value of the function $f(n)$ of the number of molecules n, we must use the rule for calculating mean values holding for continuous random variables:

$$\langle f(n) \rangle = \int f(n)\, w(n)\, dn$$
$$= \int f(n) \frac{1}{\sqrt{2\pi D}} \exp\left[-\frac{(n-\langle n \rangle)^2}{2D} \right] dn$$

The limits in the last integral as regards the meaning of the variable n cannot be smaller than 0 and greater than N, but since we assumed from the very beginning that large deviations of n from its mean value have a low probability and, as will be shown in Sec. 3.1, at large values of $\langle n \rangle$ this is indeed true, we can take minus and plus infinity, respectively, as these limits with no harm to the accuracy of our calculations, so that we finally obtain

$$\langle f(n) \rangle = \int_{-\infty}^{+\infty} f(n) \frac{1}{\sqrt{2\pi D}} \exp\left[-\frac{(n-\langle n \rangle)^2}{2D} \right] dn \quad (2.21)$$

We must note that the Gaussian distribution is often encountered in practice and describes the behaviour of very many continuous random variables, i.e. it holds not only

for the case considered above, but also for quite a few other ones. There are reasons for this. The matter is that with a large number of trials the Gaussian distribution is limiting for a whole series of distributions. There is a theorem, which owing to its importance is known as the **central limit theorem of the probability theory**, that establishes quite general conditions sufficient for a limiting distribution to be Gaussian or, as it is also called, **normal**. The widespread dispersal of the normal law of probability distribution provided the grounds for the witty remark that physicists consider the large-scale dispersal of the normal law to be a mathematical theorem, whereas mathematicians consider it to be an experimentally established fact. It must be borne in mind, naturally, that the Gaussian distribution, although encountered quite frequently, is not the only one possible.

If a continuous random variable obeys a normal distribution, the probability d*W of the fact that the values of this random variable z are confined within the interval from z to z* + d*z is determined by the formula*

$$dW(z) = \frac{1}{\sqrt{2\pi D}} \exp\left[-\frac{(z - \langle z \rangle)^2}{2D} \right] dz \qquad (2.22)$$

where $\langle z \rangle$ *is the mean value, and* D *is the dispersion of the random variable* z.

In concluding, we shall compare the Gaussian approximating formula (2.19) with the binomial distribution. Figure 1.6 shows the binomial distribution for $N = 6$ and $\Delta\tau/V = 0.5$. The results of calculating the same quantities by (2.19) are shown by crosses ($\langle n \rangle = N\Delta\tau/V = 3$, and $D = N\Delta\tau/\{V [1 - (\Delta\tau/V)]\} = 1.51$). A glance at the figure shows that even in this case, when $\langle n \rangle$ and $N - \langle n \rangle$ are not at all large, close results are obtained. At larger values of $\langle n \rangle$ and $N - \langle n \rangle$, the difference between the calculation by the accurate formula of a binomial distribution and the Gaussian formula is extremely insignificant.

2.5. Probability as a Measure of Unexpectedness

The probability of an event can be a measure of its un-expectedness. This is quite evident qualitatively. If the probability is low, an event happens rarely and, consequent-

ly, relates to the category of unexpected ones. Conversely, if the probability is close to unity, an event happens often, and from this viewpoint relates to commonplace ones.

In the theory of information, *it was agreed to take as a measure of unexpectedness of an event the natural logarithm of its probability W with the opposite sign:* —ln *W*.

The measure of unexpectedness chosen in this way transmits quite well many of our intuitive notions of the properties which it must possess. Indeed, the probability is a quantity less than unity and, consequently, its logarithm taken with the minus sign is positive, in other words, unexpectedness is a positive quantity. If an event is certain to happen, the probability is unity, and its logarithm is zero, so that the unexpectedness of a certain event happening is zero. Finally, if an event consists of two independent simple ones, since its probability equals the product of the probabilities, the unexpectedness of a complicated event equals the sum of the unexpectednesses of the simple events it consists of.

Let us consider an example for illustration. Assume that a vessel contains three molecules and that we have separated a volume in it amounting to 0.1 of the total volume, i.e. $\Delta\tau/V = 0.1$. What is the unexpectedness of the fact that this volume will contain all three molecules? The probability of the event we are interested in, according to the binomial distribution (see also Table 1.1) is

$$W\,(3) = \left(\frac{\Delta\tau}{V}\right)^3 = 10^{-3}$$

It thus follows that its unexpectedness is

$$-\ln W\,(3) = 3 \ln 10 = 6.9$$

The same result could be obtained in a somewhat different way. The event considered consists in the happening of three independent events, namely, the getting of each of the three molecules into $\Delta\tau$. The unexpectedness of one molecule getting in, since the probability of this event is $W = \Delta\tau/V = 0.1$, is

$$-\ln W = \ln 10 = 2.3$$

The unexpectedness of three molecules getting in is three times greater, i.e. we obtain the same result.

Since the ratio $\Delta\tau/V$ is small, the probability of molecules getting into $\Delta\tau$ is very low, and it will therefore be much less surprising if all three molecules are outside of $\Delta\tau$. What is the unexpectedness of this event? Since the relevant probability is

$$W\,(0) = \left(1 - \frac{\Delta\tau}{V}\right)^3 = 0.9^3$$

and taking into account that $\Delta\tau \ll 1$, we find for the unexpectedness

$$-3\ln\left(1 - \frac{\Delta\tau}{V}\right) \approx 3\,\frac{\Delta\tau}{V} = 0.3$$

Its numerical value in this case is much smaller than in the preceding one.

If the result of measurements shows that an event has happened and, for example, all three molecules were found in $\Delta\tau$, this signifies that the event has become certain and its unexpectedness is zero. Diminishing of unexpectedness that is a result of measurement can be considered as a measure of the information that was obtained because of the measurement. Since the final unexpectedness is zero, the reduction in the unexpectedness equals its original value, hence *the expression* $-\ln W\,(A)$ *is also a measure of the amount of information obtained in an experiment, which shows that the event* A *has happened.*

2.6. Entropy and Randomness

In the preceding section, we introduced a measure of unexpectedness for a random event. Assume that we are considering a complete set of mutually exclusive events. Each of these events has its own unexpectedness, and what we would like to do is to find a characteristic that is common for the entire system. Such a characteristic, known as the **entropy** or the **information entropy**, is introduced as the mean value of the unexpectednesses for the entire system, i.e. the unexpectedness of each i-th event is multiplied by the probability of this event W_i, and all the results obtained are summated. Hence, designating the entropy by S, we can write a mathematical expression defining this quantity:

$$S = -\sum_{i=1}^{N} W_i \ln W_i \tag{2.23}$$

where summation is performed over all the events forming
the complete set. The entropy characterizes the degree of
indeterminacy or randomness occurring in a given situation.
To explain this meaning of entropy, let us turn to the pre-
viously considered example, in which the molecule A in
a vessel having the volume V may or may not get into the
earmarked volume $\Delta\tau$.

Let us first assume that the volume $\Delta\tau$ is very small in
comparison with V. It is intuitively obvious that in this
case the indeterminacy of the situation is very small because
the molecule almost certainly will be outside $\Delta\tau$. The
entropy reflects this notion. Indeed, the probability of
getting into $\Delta\tau$ is $W_1 = \Delta\tau/V$, and the probability of not
getting into it is $W_2 = 1 - W_1 = 1 - (\Delta\tau/V)$. For the
entropy, consequently, we have

$$S = -\frac{\Delta\tau}{V}\ln\frac{\Delta\tau}{V} - \left(1 - \frac{\Delta\tau}{V}\right)\ln\left(1 - \frac{\Delta\tau}{V}\right)$$

If $\Delta\tau/V$ is very small, one factor in the first term tends to
zero and the other one to $-\infty$. Since, however, $-\ln(\Delta\tau/V)$
grows very slowly with diminishing of $\Delta\tau/V$, when $(\Delta\tau/V) \rightarrow$
$\rightarrow 0$ the product tends to zero*. In the second term, the
first factor tends to unity, and the second one to zero so that
when $\Delta\tau/V$ is small it is also very small. Hence, at a low
value of $\Delta\tau/V$, the value of the entropy is low.

It is not difficult to see that matters are exactly the same
when the volume $\Delta\tau$ is close to V. In this case, the molecule A
will almost certainly be in $\Delta\tau$. The indeterminacy of the
situation is small, and the value of the entropy is again
close to zero.

Then when is the greatest indeterminacy reached? Let us
attempt to answer this question after establishing the condi-
tions in which the entropy reaches its maximum value and
considering it as a function of the probability $W_1 = \Delta\tau/V$.
Using the general rule of finding the maximum of a function,
we differentiate S with respect to the probability and equate

---

* According to L'Hospital's rule, we have

$$\lim_{x\to 0}(x\ln x) = \lim_{x\to 0}\left[\frac{\dfrac{d\ln x}{dx}}{\dfrac{d}{dx}\left(\dfrac{1}{x}\right)}\right] = \lim_{x\to 0}\left[\frac{(1/x)}{-(1/x^2)}\right] = \lim_{x\to 0}(-x) = 0$$

the derivative to zero. This yields

$$\frac{dS}{dW_1} = \frac{d}{dW_1} \left[-W_1 \ln W_1 - (1 - W_1) \ln (1 - W_1) \right]$$

$$= -\ln W_1 - 1 + \ln (1 - W_1) + 1 = 0 \qquad (2.24)$$

It follows from this equation that $W_1 = (1 - W_1)$, or

$$W_1 = \frac{\Delta \tau}{V} = \frac{1}{2} \qquad (2.25)$$

Hence, the most indeterminate state is achieved when $\Delta \tau$ is half of the volume V.

Therefore, *a measure of the indeterminacy or randomness of a situation characterized by a complete set of mutually exclusive events with the probabilities W_i is a function of these probabilities* (2.23) *called the **information entropy.***

Part II

CLASSICAL STATISTICS
OF EQUILIBRIUM STATES

Chapter 3

MAXWELL DISTRIBUTION

3.1. Distribution of Particles in Space in the Absence of External Force Fields

If external force fields are absent, particles, for instance the molecules of an ideal gas, are distributed over the volume of a vessel uniformly. Indeed, in Sec. 1.2 we dealt with the considerations according to which we may consider that the probability of a molecule being in the volume $\Delta\tau$ forming a part of the vessel's volume V equals $\Delta\tau/V$ and does not depend on the shape and position of this volume. The mean number of molecules in $\Delta\tau$ with their total number equal to N is determined by relation (2.7)

$$\langle n \rangle = \frac{N\Delta\tau}{V}$$

and, consequently, is identical for any volumes $\Delta\tau$ equal in size. In other words, the mean value of the concentration, i.e. the number of molecules in unit volume ($\Delta\tau = 1$), is a constant quantity.

The equality of the mean values of the concentration does not signify that at any instant the numbers of molecules in the volume $\Delta\tau$ and in the volume $\Delta\tau'$ equal to it are the same. On the contrary, the true number of molecules n, as a rule, differs from $\langle n \rangle$ and is different for these two identical but non-coinciding volumes. Deviations of the number of molecules from the mean value are known as **fluctuations**. It is not difficult to show that in the majority of cases of interest from a practical viewpoint, the fluctua-

tions are very small and may be disregarded. To convince ourselves in the truth of this statement, let us consider an example.

Let a vessel with a volume of $V = 10$ cm^3 contain an ideal gas having a total of $N = 2.69 \times 10^{20}$ molecules, which corresponds to standard temperature and pressure (S.T.P.— a temperature of 0 °C and atmospheric pressure). Let us mentally separate a part of this volume, $\Delta\tau$, forming one per cent of V, i.e. $\Delta\tau = 0.1$ cm^3. The mean number of molecules in $\Delta\tau$ is $\langle n \rangle = 0.01N = 2.69 \times 10^{18}$, while the mean number of molecules outside this volume is $N -$ $- \langle n \rangle \approx 2.66 \times 10^{20}$. As we showed in Sec. 2.4, at such large values of the numbers $\langle n \rangle$ and $N - \langle n \rangle$, the number of molecules n in the volume $\Delta\tau$ may be considered as a continuous random variable whose probability density is determined by the Gaussian distribution (2.20). It is a simple matter to calculate the probability of any deviation from the mean value. Let us calculate, for example, the probability of the fact that the number of molecules in $\Delta\tau$ in the above example will differ from the mean value by more than 0.01%. In other words, we are interested in the probability of n being either smaller than $\langle n \rangle (1 - 10^{-4})$ or larger than $\langle n \rangle (1 + 10^{-4})$. The corresponding probability is

$$W = \int_{-\infty}^{\langle n \rangle (1-10^{-4})} \frac{1}{\sqrt{2\pi D}} \exp\left[- \frac{(n-\langle n \rangle)^2}{2D} \right] dn$$

$$+ \int_{\langle n \rangle (1+10^{-4})}^{\infty} \frac{1}{\sqrt{2\pi D}} \exp\left[- \frac{(n-\langle n \rangle)^2}{2D} \right] dn$$

If we designate $n - \langle n \rangle$ by Δn, we have

$$W = \int_{-\infty}^{-10^{-4}\langle n \rangle} \frac{1}{\sqrt{2\pi D}} \exp\left(- \frac{\Delta n^2}{2D} \right) d(\Delta n)$$

$$+ \int_{10^{-4}\langle n \rangle}^{\infty} \frac{1}{\sqrt{2\pi D}} \exp\left(- \frac{\Delta n^2}{2D} \right) d(\Delta n)$$

The integrand function is even, and therefore both integrals, which are taken in symmetric limits, equal each other,

so   that

$$W = 2 \int\limits_{10^{-4}\langle n\rangle}^{\infty} \frac{1}{\sqrt{2\pi D}} \exp\left(-\frac{\Delta n^2}{2D}\right) \mathrm{d}\,(\Delta n)$$

Similar integrals are encountered in statistics quite frequently, and it will therefore be good to consider their evaluation in greater detail. First of all, we introduce the new variable $x = \Delta n/\sqrt{D}$ and the notation $x_0 = 10^{-4} \times \times \langle n\rangle/\sqrt{D}$. Hence,

$$W = \frac{2}{\sqrt{2\pi}} \int\limits_{x_0}^{\infty} \exp\left(-\frac{x^2}{2}\right) \mathrm{d}x$$

The   function

$$\mathrm{erf}\,(x_0) = \frac{2}{\sqrt{2\pi}} \int\limits_0^{x_0} \exp\left(-\frac{x^2}{2}\right) \mathrm{d}x \qquad (3.1)$$

is called the **probability integral** or the **error function**, and tables of its values are given in the mathematical literature; see, for example, Abramovitz and Stegun [12], or Beyer [13]. The error function $\mathrm{erf}\,(x_0)$ determines the probability of the fact that the random variable x distributed according to the Gaussian law is less than x_0. If $x_0 = \infty$, then as is evident from the meaning of the error function, we have

$$\mathrm{erf}\,(\infty) = \frac{2}{\sqrt{2\pi}} \int\limits_0^{\infty} \exp\left(-\frac{x^2}{2}\right) \mathrm{d}x = 1$$

Now   we   can   write

$$W = \frac{2}{\sqrt{2\pi}} \int\limits_0^{\infty} \exp\left(-\frac{x^2}{2}\right) \mathrm{d}x$$

$$-\frac{2}{\sqrt{2\pi}} \int\limits_0^{x_0} \exp\left(-\frac{x^2}{2}\right) \mathrm{d}x = 1 - \mathrm{erf}\,(x_0) \qquad (3.2)$$

Therefore, it is simple to calculate W if we have at our disposal tables of the error functions. When $x_0 \leqslant 1$ or, conversely, $x_0 \gg 1$, the value of the error function can also be found without the aid of tables. It is shown in Appendix 1

that when $x_0 \leqslant 1$, we have

$$\text{erf}(x_0) \approx \frac{2}{\sqrt{2\pi}}\, x_0 \tag{3.3}$$

while when $x_0 \geqslant 2$, the error function is assessed by the formula

$$\text{erf}(x_0) \approx 1 - \frac{2}{\sqrt{2\pi}}\, \frac{1}{x_0} \exp\left(-\frac{x_0^2}{2}\right) \tag{3.4}$$

Let us use the results obtained to calculate the probabilities we are interested in. Since the dispersion, as follows from the formula given in the last paragraph of Sec. 2.4, is

$$D = N\frac{\Delta\tau}{V}\left(1 - \frac{\Delta\tau}{V}\right) = \langle n \rangle \left(1 - \frac{\langle n \rangle}{N}\right) \approx \langle n \rangle$$

then

$$x_0 = \frac{10^{-4}\langle n \rangle}{\sqrt{D}} = 10^{-4}\sqrt{\langle n \rangle}$$

When $\langle n \rangle = 2.69 \times 10^{18}$, this yields $x_0 = 1.64 \times 10^5$, so that relation (3.4) may be applied with a very high accuracy. From (3.2) with the aid of (3.4), we find

$$W = \frac{2}{\sqrt{2\pi}}\, \frac{1}{x_0} \exp\left(-\frac{x_0^2}{2}\right) \tag{3.5}$$

i.e. the numerical value of W has an order of $\exp(-1.35 \times 10^{10}) = 10^{-0.58 \times 10^{10}}$.

It is difficult to conceive how small the probability of the considered event is. For illustration, we can compare it with the probability of the fact that a monkey seated at a typewriter would type in the required order and with no errors the complete text of Lev Tolstoi's *War and Peace* (an example proposed by E. Borel). In one edition of the novel, its three volumes contained 2330 pages. If we assume that a page has 45 lines, and a line has a total of 50 characters and spaces (i.e. 50 symbols), the total number of symbols in the novel is about 5.25×10^6. Since it is assumed that the monkey presses all the keys at random, the probability of its pressing a given specific key is 1/50 (the number of keys totals 50). Considering all the symbols to be typed independently, it is a simple matter to obtain the following value for the required probability:

$$W = \left(\frac{1}{50}\right)^{5.25 \times 10^6} = 10^{-8.9 \times 10^7}$$

i.e. it is $10^{0.57 \times 10^{10}}$ times greater than the probability of the insignificant increase in the concentration of the molecules in the volume $\Delta\tau$ that we have considered!

Consequently, *in the absence of external forces, the mean concentration of particles is identical over the entire vessel, and the true concentration may be considered equal to its mean value because even a very small deviation from the mean value has a negligible probability owing to the large number of particles.*

It is very important for the correctness of the conclusion we have made that the number of particles be large. If, for instance, we consider that the volume $\Delta\tau = 10^{-3}$ $\mu m^3 = 10^{-15}$ cm^3, the mean number of particles in it will be $\langle n \rangle = 2.69 \times 10^4$, i.e. much smaller than in the preceding case. The dispersion has the value $D = \langle n \rangle$. The probability of the concentration deviating from its mean value by an amount greater than 0.01% will be determined by expression (3.1), but with a different value of the parameter x_0, namely,

$$x_0 = \frac{10^{-4} \langle n \rangle}{\sqrt{D}} = 10^{-4} \sqrt{\langle n \rangle} = 1.64 \times 10^{-2}$$

Since the value of x_0 is much smaller than unity, we can find with the aid of (3.2) and (3.3) that

$$W = 1 - \sqrt{\frac{2}{\pi}}\, x_0 = 0.984$$

i.e. the event is virtually certain. Deviations of the concentration by more than 10% from the mean value, however, have a low probability. Indeed, in this case we have

$$x_0 = \frac{10^{-1} \langle n \rangle}{\sqrt{D}} = 10^{-1} \sqrt{\langle n \rangle} = 16.4$$

and by (3.5)

$$W = \frac{2}{\sqrt{2\pi}} \frac{1}{16.4} \exp\left(-\frac{16.4^2}{2}\right) = 1.9 \times 10^{-60}$$

Hence, in small volumes containing a comparatively insignificant number of particles, the relative fluctuations may be appreciable. In some phenomena, they play a very important role. Particularly, the scattering of the Sun's light by the atmosphere and the sky's blue colour are explained by

fluctuations of the density of the air. The colour of the sky is associated with the fact that solar radiation with a shorter wavelength (blue) is scattered more effectively than red radiation having a longer wavelength.

3.2. Probability Density for Momenta of Molecules

Having solved the problem of how particles (molecules) are distributed in space, we can interest ourselves in the possible values of their velocity $\mathbf{v}$ or momentum $\mathbf{p} = m_0\mathbf{v}$ (here m_0 is the mass of a particle). Actually, molecules with the most diverse values of their momentum are encountered
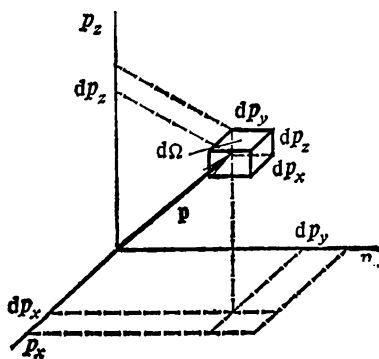
Fig. 3.1

in a gas, and for this reason from the viewpoint of the theory of probability it is only necessary to know the probability of its different values. In other words, in statistics, the momentum of the molecules in a vessel is treated as a continuous random variable, and to characterize it we must know the relevant probability density, which we shall designate by w_p.

For our further treatment, it is convenient to introduce the notion of momentum space. Let us lay off the components of a molecule's momentum along the axes of a Cartesian system of coordinates (Fig. 3.1). If we are interested in the probability dW of the components of the momentum of a definite molecule being confined in the intervals from p_x

to $p_x + \mathrm{d}p_x$, from p_y to $p_y + \mathrm{d}p_y$, and from p_z to $p_z + \mathrm{d}p_z$, we can formulate these conditions graphically with the aid of the momentum space. The imposed requirements signify from a geometric viewpoint that the tip of the momentum vector drawn from the origin of coordinates gets into the elementary rectangular volume $\mathrm{d}\Omega$ in the momentum space depicted in Fig. 3.1. Since the sides of the volume are $\mathrm{d}p_x$, $\mathrm{d}p_y$, and $\mathrm{d}p_z$, respectively, then

$$\mathrm{d}\Omega = \mathrm{d}p_x\,\mathrm{d}p_y\,\mathrm{d}p_z \qquad (3.6)$$

The probability $\mathrm{d}W$ we are interested in can be written as $\mathrm{d}W = w_p\,\mathrm{d}\Omega$, where w_p is the momentum's probability density that has to be found.

To establish the form of w_p, it is sufficient, as was first shown by Maxwell, to use the following assumptions:

(a) all directions in space are equivalent and therefore any direction of motion of a particle, i.e. any direction of its momentum, is equally probable. This property is sometimes called the property of **isotropy** of the probability density w_p;

(b) the motions along the three mutually perpendicular axes are *independent*, i.e. the value of x—the momentum component p_x—does not depend on what are the values of the components p_y and p_z.

The second condition is less obvious than the first one and is simply not correct if we take into account motion at a velocity close to that of light, i.e. the effects of the theory of relativity. Indeed, since according to the theory of relativity motion at a velocity greater than that of light is impossible, this signifies that the velocity components along the different axes are related to one another by the inequality

$$v_x^2 + v_y^2 + v_z^2 \leqslant c^2$$

For example, if $v_x \approx c$, this is possible only when $v_y \approx$ $\approx v_z \approx 0$. We must thus be ready for the fact that the conclusions arrived at on the basis of the adopted assumptions will not satisfy the requirements of the theory of relativity.

To approach the solution of the problem we have posed, let us consider the probability density for *one* of the momentum components, for instance p_x. The probability

dW_{p_x} of the component p_x being within the interval from p_x to $p_x + dp_x$ can be written in the form

$$dW_{p_x} = w_{p_x}\, dp_x \tag{3.7}$$

where w_{p_x} is the probability density for p_x. Since an identical probability of the values of the components p_x and $-p_x$ follows from the property of isotropy, the probability density w_{p_x} is an even function, i.e. it depends on the square of p_x:

$$w_{p_x} = \varphi\,(p_x^2) \tag{3.8}$$

According to the same property of isotropy, the probability densities of the two other components are expressed in a similar way:

$$w_{p_y} = \varphi\,(p_y^2) \quad \text{and} \quad w_{p_z} = \varphi\,(p_z^2) \tag{3.8'}$$

where φ is the same function. Using the independence of the components, we can readily express the probability density $w_{\mathbf{p}}$ in terms of the probability densities w_{p_x}, w_{p_y}, and w_{p_z}. Indeed, the probability of the momentum $\mathbf{p}$ getting into the volume element $d\Omega = dp_x\, dp_y\, dp_z$ of the momentum space is

$$dW = w_{\mathbf{p}}\ d\Omega \tag{3.9}$$

On the other hand, this event is equivalent to the fact that the component p_x is within the interval from p_x to $p_x + dp_x$, the component p_y is within the interval from p_y to $p_y + dp_y$, and the component p_z is within the interval from p_z to $p_z + dp_z$. Owing to the independence of the enumerated events, the probability (3.9) can be written as a product:

$$w_{\mathbf{p}}\, d\Omega = w_{p_x}\, dp_x \cdot w_{p_y}\, dp_y \cdot w_{p_z}\, dp_z$$

$$= \varphi\,(p_x^2) \cdot \varphi\,(p_y^2) \cdot \varphi\,(p_z^2)\, dp_x\, dp_y\, dp_z$$

If we take (3.6) into account, it follows from the last equation that

$$w_{\mathbf{p}} = \varphi\,(p_x^2)\, \varphi\,(p_y^2)\, \varphi\,(p_z^2)$$

Since the probability density $w_{\mathbf{p}}$ should not depend on the direction of the momentum (the property of isotropy), it therefore depends only on its magnitude, i.e.

$$w_{\mathbf{p}} = \psi\,(p_x^2 + p_y^2 + p_z^2) = \psi\,(p^2)$$

where ψ is a function that is also meanwhile unknown. From the last two equations, we obtain the following relation:

$$\psi\left(p^2\right) = \varphi\left(p_x^2\right)\varphi\left(p_y^2\right)\varphi\left(p_z^2\right) \tag{3.10}$$

The condition (3.10) allows us to determine the form of the unknown functions φ and ψ, i.e. to find the probability densities w_p and w_{p_x}. To do this, let us take logarithms of (3.10):

$$\ln\psi = \ln\varphi\left(p_x^2\right) + \ln\varphi\left(p_y^2\right) + \ln\varphi\left(p_z^2\right)$$

We now differentiate this identity with respect to p_x:

$$\frac{\psi'}{\psi}2p_x = \frac{\varphi'}{\varphi}2p_x \tag{3.11}$$

where the prime stands for the derivative of the relevant function with respect to its compound argument, i.e.

$$\psi'\left(z\right) = \frac{d\psi}{dz}, \quad \varphi'\left(z\right) = \frac{d\varphi}{dz}$$

After cancelling $2p_x$ from (3.11), we obtain

$$\frac{\psi'\left(p^2\right)}{\psi\left(p^2\right)} = \frac{\varphi'\left(p_x^2\right)}{\varphi\left(p_x^2\right)} \tag{3.12}$$

In absolutely the same way, differentiating with respect to p_y or p_z, we can obtain two other similar relations:

$$\frac{\psi'\left(p^2\right)}{\psi\left(p^2\right)} = \frac{\varphi'\left(p_y^2\right)}{\varphi\left(p_y^2\right)}, \quad \frac{\psi'\left(p^2\right)}{\psi\left(p^2\right)} = \frac{\varphi'\left(p_z^2\right)}{\varphi\left(p_z^2\right)} \tag{3.12'}$$

It follows from (3.12) and (3.12') that

$$\frac{\varphi'\left(p_x^2\right)}{\varphi\left(p_x^2\right)} = \frac{\varphi'\left(p_y^2\right)}{\varphi\left(p_y^2\right)} = \frac{\varphi'\left(p_z^2\right)}{\varphi\left(p_z^2\right)}$$

Since the first ratio depends only on p_x, the second only on p_y, and the third only on p_z, the above equality observed identically for all values of p_x, p_y, and p_z can hold only when these ratios do not indeed depend on the relevant arguments, i.e. are constant numbers. Designating the constant by $-\beta$, we obtain a differential equation determining the function φ:

$$\frac{\varphi'}{\varphi} = -\beta$$

The solution of this equation has the form

$$\varphi \ (p_x^2) = C \exp \ (-\beta p_x^2)$$

where C is a second unknown constant. If the function φ is known, the function ψ is determined by Eq. (3.10).

Hence, *it follows from the condition of isotropy and the condition of the independence of motion along mutually perpendicular axes that the probability* dW_{p_x} *of the momentum component* p_x *being within the interval from* p_x *to* $p_x + dp_x$ *is determined by the relation*

$$dW_{p_x} = C \exp \left(- \beta p_x^2 \right) dp_x \qquad (3.13)$$

(similarly for the other components), and the probability dW *of the momentum being within the volume* $d\Omega$, *by the relation*

$$dW = C^3 \exp \ (-\beta p^2) \ d\Omega \qquad (3.14)$$

where C and β are constants that must be determined with the aid of additional conditions.

3.3. Normalization Condition

One of the conditions for determining the constants C and β follows from the requirement that the integral of the probability density over all possible values of the argument (having the meaning of the probability of the fact that the momentum of a molecule has one of the possible values) be equal to unity. This condition is known as the **normalization condition** and is written as follows:

$$\int_{-\infty}^{+\infty} w_{p_x} \, dp_x = \int_{-\infty}^{+\infty} C \exp \left(- \beta p_x^2 \right) dp_x = 1 \qquad (3.15)$$

The normalizing relation (3.15) can be considered as an equation from which the constant C is determined in terms of the constant β:

$$C = \left[\int_{-\infty}^{+\infty} \exp \ (-\beta p_x^2) \ dp_x \right]^{-1} \qquad (3.16)$$

A glance at (3.16) shows, particularly, that the constant β must be positive because otherwise the integral in (3.16)

diverges, and the constant C becomes equal to zero. The integral in (3.16) is evaluated in Appendix 2. The result is as follows:

$$C = \sqrt{\frac{\beta}{\pi}} \qquad (3.17)$$

Hence, *the value of the normalization constant is determined in terms of the parameter* β *with the aid of relation* (3.17).

3.4. Relation Between the Maxwell Distribution Parameter β and the Temperature

To complete the determination of the probability density for the momenta of molecules, it remains for us to find the value of the parameter β. Since this quantity depends on the conditions in which a gas is, it can be found only by considering a specific physical situation. Assume, for instance, that we have an ideal monatomic gas. Its internal energy U is determined by the relation

$$U = \frac{3}{2} \frac{M}{\mu} RT \qquad (3.18)$$

where M is the mass of the gas, μ is its molar mass, R is the molar gas constant, and T is the absolute temperature. Customarily, the heat capacity at constant volume C_V is determined experimentally. It is constant for a monatomic gas and equals

$$C_V = \frac{M}{\mu} \frac{3}{2} R$$

It is known from thermodynamics (see Chap. 5) that the heat capacity is related to the internal energy by the expression

$$U = \int_0^T C_V \, dT$$

from which relation (3.18) follows in the given case.

The internal energy of an ideal monatomic gas is the mean value of the kinetic energy of the translational motion of all its molecules because for such a gas the interaction of the molecules with one another (i.e. their mutual potential energy) may be disregarded.

The kinetic energy of an individual molecule is

$$\varepsilon = \frac{p^2}{2m_0} \qquad (3.19)$$

where m_0 is the mass of a molecule. Using the properties of mean values, we can write the mean value of the energy as follows:

$$\langle \varepsilon \rangle = \frac{\langle p^2 \rangle}{2m_0} = \frac{1}{2m_0} \left(\langle p_x^2 \rangle + \langle p_y^2 \rangle + \langle p_z^2 \rangle \right)$$

It can be seen from the property of isotropy that the mean values of the squares of all the components are the same, so that

$$\langle \varepsilon \rangle = \frac{3}{2} \frac{1}{m_0} \langle p_x^2 \rangle = \frac{3}{2} \frac{1}{m_0} \langle p_y^2 \rangle = \frac{3}{2} \frac{1}{m_0} \langle p_z^2 \rangle$$

The quantity

$$\langle p_x^2 \rangle = \int\limits_{-\infty}^{+\infty} p_x^2 C \exp\left(-\beta p_x^2 \right) \, \mathrm{d}p_x$$

Since C is determined by relation (3.17), and the integral is evaluated by the formula derived in Appendix 2, for the quantity $\langle p_x^2 \rangle$ we obtain

$$\langle p_x^2 \rangle = \sqrt{\frac{\beta}{\pi}} \, \frac{\sqrt{\pi}}{2} \, \beta^{-3/2} = \frac{1}{2\beta}$$

If the mass M of a gas and its molar mass μ are given, the number of moles is M/μ and, consequently, the total number of gas molecules is

$$N = \frac{M}{\mu} N_A$$

where N_A is **Avogadro's constant**, i.e. the number of molecules in one mole.

The mean value of the energy of a gas is the sum of the mean values of the energies of all its molecules, and for this reason the internal energy of an ideal monatomic gas is

$$U = N \langle \varepsilon \rangle = N \frac{3}{2} \frac{\langle p_x^2 \rangle}{m_0} = \frac{3}{2} \frac{N}{m_0} \frac{1}{2\beta} = \frac{M}{\mu} N_A \frac{3}{2} \frac{1}{2m_0\beta}$$

Comparing the last relation with (3.18), we find that

$$\beta = \frac{N_A}{2Rm_0T}$$

The ratio of the molar gas constant to Avogadro's constant is the **Boltzmann constant** k, and for this reason *the parameter* β *contained in the density of the probability of the momentum values* (3.13) *or* (3.14) *and called the Maxwell probability density is*

$$\beta = \frac{1}{2m_0 kT} \qquad (3.20)$$

i. e. is determined by the absolute temperature.

3.5. Maxwell Probability Density for Momenta

The results obtained in the preceding sections show that *the probability densities of the momentum values* (*the Maxwell probability densities*) *are expressed by the following formulas:*

$$\left.\begin{aligned}
w_{p_x}\, dp_x &= (1/\sqrt{2\pi m_0 kT}) \exp\left[-p_x^2/(2m_0 kT)\right]\, dp_x \\
w_{p_y}\, dp_y &= (1/\sqrt{2\pi m_0 kT}) \exp\left[-p_y^2/(2m_0 kT)\right]\, dp_y \\
w_{p_z}\, dp_z &= (1/\sqrt{2\pi m_0 kT}) \exp\left[-p_z^2/(2m_0 kT)\right]\, dp_z \\
w_{\mathbf{p}}\, d\Omega &= [1/\sqrt{(2\pi m_0 kT)^3}] \exp\left[-p^2/(2m_0 kT)\right]\, d\Omega
\end{aligned}\right\} \qquad (3.21)$$

Let us consider one of the momentum components, for instance p_x, in greater detail. Comparing the probability density of this random variable with (2.22), we can readily see that it obeys the Gaussian distribution or, as is customarily said, the normal distribution. The mean value of the component is zero, and its dispersion coincides with the mean value of p_x^2:

$$D = \langle p_x^2 \rangle = m_0 kT \qquad (3.22)$$

Figure 3.2 shows the probability density w_{p_x} against p_x. The corresponding curve owing to w_{p_x} being even is symmetric relative to the axis of ordinates. The maximum value is achieved when $p_x = 0$ and is determined by the temperature of the gas

$$w_{p_x}|_{p_x=0} = \frac{1}{\sqrt{2\pi m_0 kT}} \qquad (3.23)$$

At

$$p_x = \sqrt{m_0 kT} \qquad (3.24)$$

i.e. at the root-mean-square value of the x-component of the momentum, the value of the probability density diminishes to $1/\sqrt{e} = 1/1.65 = 0.61$ of the maximum value and at larger values of p_x it rapidly shrinks to zero.

If we heat a gas to a higher temperature, the probability density will change. By (3.23), the maximum value will
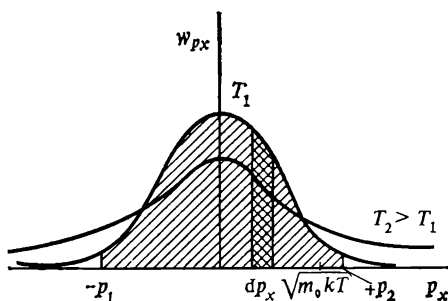
Fig. 3.2

be lower, and by (3.24), the curve itself will become wider.

Let us choose on the axis of abscissas the segment dp_x that is small in comparison with $\sqrt{m_0 k T}$. Over the length of this segment, the probability density w_{p_x} is almost constant. The probability of the value of the x-component of the momentum being within the interval dp_x is determined by the expression

$$dw = w_{p_x}\, dp_x$$

and, consequently, is depicted by the area confined by the axis of abscissas, the distribution curve, and the ordinates corresponding to the beginning and the end of the interval dp_x (cross-hatched in Fig. 3.2).

Such a geometric interpretation relates to an arbitrary, and not only to an infinitely small interval dp_x. For instance, the probability of the component p_x being larger than $-p_1$, but smaller than $+p_2$ is depicted by the hatched area in Fig. 3.2. The total area under the distribution curve naturally equals unity because it corresponds to the probability of a certain event $(-\infty < p_x < +\infty)$.

Having at our disposal the Maxwell probability density, we can solve problems of two types.

First, we can find the *mean values* of various functions of a particle's momentum. For example, for any even power of the component, we have

$$\langle p_x^{2n} \rangle = \frac{1}{\sqrt{2\pi m_0 kT}} \int\limits_{-\infty}^{+\infty} p_x^{2n} \exp\left(-\frac{p_x^2}{2m_0 kT}\right) \, dp_x$$

The corresponding integral is evaluated in Appendix 2, and we find with its aid that

$$\langle p_x^{2n} \rangle = (m_0 kT)^n \times 1 \times 3 \times 5 \ldots (2n - 1)$$

that is

$$\langle p_x^2 \rangle = m_0 kT; \quad \langle p_x^4 \rangle = 3 \, (m_0 kT)^2; \quad \langle p_x^6 \rangle = 15 \, (m_0 kT)^3 \quad (3.25)$$

For any odd power of p_x, the mean value is zero because this function takes on positive and negative values with the same frequency.

Second, we can find the *probabilities* of events. As an example, let us find the probability of the fact that the component of the momentum of a particle along the positive direction of the x-axis is greater than the value corresponding to motion with a velocity of $0.1c$ (c is the speed of light). In other words, we are interested in the area under the Maxwell distribution curve from the point $p_x = 0.1m_0 c$ to an infinitely remote point, i.e.

$$W = \int\limits_{0.1m_0 c}^{\infty} \frac{1}{\sqrt{2\pi m_0 kT}} \exp\left(-\frac{p_x^2}{2m_0 kT}\right) \, dp_x$$

If we introduce the variable $\xi = p_x / \sqrt{m_0 kT}$, we have

$$W = \frac{1}{\sqrt{2\pi}} \int\limits_{0.1m_0 c / \sqrt{m_0 kT}}^{\infty} \exp\left(-\frac{\xi^2}{2}\right) \, d\xi = \frac{1}{2} \left[1 - \mathrm{erf}\left(\frac{0.1m_0 c}{\sqrt{m_0 kT}}\right) \right]$$

and provided that

$$\xi_0 = \frac{0.1m_0 c}{\sqrt{m_0 kT}} \gg 2 \qquad (3.26)$$

we may use formula (3.4), i.e.

$$W = \frac{1}{\sqrt{2\pi}} \frac{1}{\xi_0} \exp\left(-\frac{\xi_0^2}{2}\right)$$

It is not difficult to see that in almost all practical cases, inequality (3.26) is observed. The conditions for its observance become less favourable when the mass of the particles diminishes and their temperature rises. For atomic hydrogen ($m_0 = 1.67 \times 10^{-27}$ kg) at a temperature of $T = 3000$ K, we have $\xi_0 = 6 \times 10^3$ and, consequently, $W \sim$ $\sim \exp\left(-2 \times 10^7\right)$, i.e. is a very small quantity.

Upon the explosion of an atomic bomb, the temperature of the reaction products and, particularly, of the neutrons may reach 10 million degrees. Since the mass of a neutron $m_n \approx 1.7 \times 10^{-27}$ kg, the parameter ξ_0 equals 10^2, so that in this case too the probability of velocities close to that of light is very low.

In a gas discharge, it is relatively simple to create conditions in which the electrons of the plasma have a very high temperature reaching $T = 20\,000$ K. Since the mass of an electron $m_e = 9 \times 10^{-29}$ kg, for this case $\xi_0 \approx 50$, and the probability W is again very low.

The above assessments show why the fact that the Maxwell distribution does not include effects of the theory of relativity and theoretically allows values of the velocities exceeding that of light is of no importance from a practical viewpoint.

In concluding, we shall note (this may sometimes be convenient) that the problem of finding the probability of an event may be considered formally as the finding of the mean value of a function which within a certain region equals unity, and in all the remaining space equals zero. Let us illustrate this with an example that will also help us establish the relation between the probability densities w_{p_x} and w_p. Assume that we are interested in the probability of a particle moving along the x-axis in the positive direction and are not interested in what motion is occurring here along the y- and z-axes. The required probability coincides with the probability of a positive value of the momentum's x-component, and to calculate it we may find the mean value of a function that equals unity at $p_x > 0$ and zero at $p_x < 0$:

$$\varphi(p_x) = \begin{cases} 1 & \text{at } p_x \geqslant 0 \\ 0 & \text{at } p_x < 0 \end{cases}$$

With the aid of the function $\varphi\,(p_x)$, we can write for the probability

$$W = \int\limits_{-\infty}^{+\infty} \varphi\,(p_x)\,w_{p_x}\,\mathrm{d}p_x = \int\limits_{0}^{\infty} \frac{1}{\sqrt{2\pi m_0 kT}}$$

$$\times \exp\left(-\frac{p_x^2}{2m_0 kT}\right)\mathrm{d}p_x = \frac{1}{2}$$

The same problem can be solved quite easily proceeding from the probability density $w_\mathbf{p}$. Let us write out the integral of $w_\mathbf{p}$ in the momentum space:

$$W = \int \varphi\,(p_x)\,w_\mathbf{p}\,\mathrm{d}\Omega = \int\limits_{-\infty}^{+\infty}\mathrm{d}p_y \int\limits_{-\infty}^{+\infty}\mathrm{d}p_z \int\limits_{-\infty}^{+\infty}\mathrm{d}p_x$$

$$\times \frac{\varphi\,(p_x)}{(2\pi m_0 kT)^{3/2}}\exp\left(-\frac{p_x^2+p_y^2+p_z^2}{2m_0 kT}\right)\mathrm{d}\Omega$$

The integral can be divided into the product of three integrals:

$$W = \int\limits_{-\infty}^{+\infty}\exp\left(-\frac{p_y^2}{2m_0 kT}\right)\frac{\mathrm{d}p_y}{\sqrt{2\pi m_0 kT}}$$

$$\times \int\limits_{-\infty}^{+\infty}\exp\left(-\frac{p_z^2}{2m_0 kT}\right)\frac{\mathrm{d}p_z}{\sqrt{2\pi m_0 kT}}$$

$$\times \int\limits_{-\infty}^{+\infty}\exp\left(-\frac{p_x^2}{2m_0 kT}\right)\frac{\varphi\,(p_x)}{\sqrt{2\pi m_0 kT}}\,\mathrm{d}p_x$$

Since the first two integrals equal unity according to the condition of normalization, it is evident that the same result is obtained as when using the probability density w_{p_x}. It is evident that this will always happen when we are seeking the mean value of a function depending only on the component p_x. If we want to find the mean value of a function depending on all three components p_x, p_y, and p_z, we must use the probability density $w_\mathbf{p}$.

3.6. Velocity Distribution

In practical applications, it is often necessary to find the probability of particles having certain velocity values, or the mean value of a quantity depending on the velocity. These problems can be solved with the aid of the Maxwell probability density for momenta if the velocities are first converted to momenta as was done, for example, in the preceding section, where we actually determined the probability of a particle's velocity being greater than $0.1c$.

It is convenient, however, to also have the Maxwell probability density for the velocity so as not to perform the preliminary conversion. Let us designate the probability density for the x-component of the velocity v_x by w_{v_x}. The probability of v_x being within the interval dv_x is therefore determined by the formula

$$dW = w_{v_x}\,dv_x$$

This probability can also be expressed in terms of the probability density of the x-component of the momentum if only the interval dp_x is chosen so that it corresponds to dv_x:

$$dW = w_{p_x}\,dp_x$$

Since the momentum and the velocity are related by the expression $p_x = m_0 v_x$, it is obvious that correspondence occurs if $dp_x = m_0\,dv_x$. Introducing the value of p_x expressed in terms of the velocity into the probability density w_{p_x}, we find

$$dW = w_{v_x}\,dv_x = w_{p_x}\,(m_0 v_x)\,m_0\,dv_x$$

$$= \frac{m_0}{\sqrt{2\pi m_0 kT}}\exp\left(-\frac{m_0 v_x^2}{2kT}\right)dv_x$$

Hence, *the probability of the x-component v_x of the velocity being within the interval of values from v_x to $v_x + dv_x$ is determined by the following form of the Maxwell distribution:*

$$dW = w_{v_x}\,dv_x = \sqrt{\frac{m_0}{2\pi kT}}\exp\left(-\frac{m_0 v_x^2}{2kT}\right)dv_x \qquad (3.27)$$

Similar expressions hold for the other components:

$$\left.\begin{array}{l} w_{v_y}\, \mathrm{d}v_y = \sqrt{\dfrac{m_0}{2\pi kT}}\, \exp\left(-\dfrac{m_0 v_y^2}{2kT} \right) \mathrm{d}v_y \\[3mm] w_{v_z}\, \mathrm{d}v_z = \sqrt{\dfrac{m_0}{2\pi kT}}\, \exp\left(-\dfrac{m_0 v_z^2}{2kT} \right) \mathrm{d}v_z \end{array}\right\} \qquad (3.27')$$

Owing to the independence of the values of the velocity components along different axes, the probability density for a random velocity vector is obtained by multiplying the written out probability densities:

$$w_{\mathbf{v}}\, \mathrm{d}v_x\, \mathrm{d}v_y\, \mathrm{d}v_z = \left(\frac{m_0}{2\pi kT} \right)^{3/2} \exp\left(-\frac{m_0 v^2}{2kT} \right) \mathrm{d}v_x\, \mathrm{d}v_y\, \mathrm{d}v_z \quad (3.28)$$

Note that the probability density w_{v_x} is not obtained by substituting $m_0 v_x$ instead of p_x into the probability density for the x-component of the momentum, but that the additional factor m_0 associated with the transition from $\mathrm{d}p_x$ to $\mathrm{d}v_x$ is also needed. In a transition to new variables, it is always necessary to transform the probability $\mathrm{d}W$, and not the separately taken probability density.

3.7. Magnitude of Momentum and Energy Distribution

It is sometimes more convenient to deal with the momentum set by its magnitude and the angles θ and φ characterizing its direction (Fig. 3.3) instead of by its projections onto the rectangular axes of the momentum space. This corresponds to a transition to a spherical system of coordinates in which a vector is determined by its length, the angle θ with the p_z-axis coinciding in direction with the z-axis in conventional space, and the angle φ between the projection of the vector $\mathbf{p}$ onto the plane $p_x O p_y$ and the p_x-axis. A volume element in spherical coordinates (Fig. 3.3) has the following value:

$$\mathrm{d}\Omega = \mathrm{d}p \cdot p\, \mathrm{d}\theta \cdot p \sin\theta\, \mathrm{d}\varphi = p^2 \sin\theta\, \mathrm{d}p\, \mathrm{d}\theta\, \mathrm{d}\varphi \quad (3.29)$$

The probability of the momentum vector terminating in $\mathrm{d}\Omega$ is determined by the product of the probability density w_p transformed to the new coordinates and the transformed

volume element (3.29):

$$dW = \frac{1}{(2\pi m_0 kT)^{3/2}} \exp\left(-\frac{p^2}{2m_0 kT}\right) p^2 \sin\theta \, dp \, d\theta \, d\varphi \quad (3.30)$$

Assume that we are interested in the probability dW of the magnitude of a particle's momentum being confined within the interval from p to $p + dp$, and are not interested
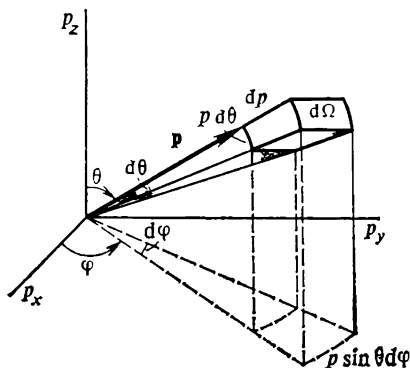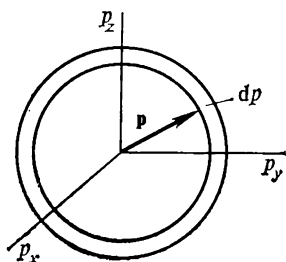
Fig. 3.3   Fig. 3.4

in the direction of this momentum. If we designate the probability density for the magnitude of the momentum by w_p, according to the definition of the probability density, we have

$$dW = w_p \, dp$$

Since, on the other hand, this probability equals the probability of a particle's momentum being inside a spherical layer of radius p and thickness dp (Fig. 3.4), dW is the sum of $w_p \, d\Omega$ over all the volume elements $d\Omega$ forming the spherical layer. Since the layer is infinitely thin, at all its points the momentum has an identical value of its magnitude, and for this reason the probability density w_p is constant too. Here the probability dW equals the probability density w_p multiplied by the volume $4\pi p^2 \, dp$ of the spherical layer so that

$$dW = \frac{4\pi p^2}{(2\pi m_0 kT)^{3/2}} \exp\left(-\frac{p^2}{2m_0 kT}\right) dp$$

Hence, *the probability density* w_p *of values of the magnitude of the momentum is determined by the relation*

$$w_p \, dp = \frac{4\pi p^2}{(2\pi m_0 kT)^{3/2}} \exp\left(-\frac{p^2}{2m_0 kT}\right) dp \qquad (3.31)$$

Formula (3.31) can also be obtained formally with no difficulty. Let us write the integral

$$dW = \int w_p \, d\Omega$$

in which integration is performed over a spherical layer of thickness dp. Using (3.30), we obtain

$$dW = \int\limits_{p}^{p+dp} dp \int\limits_{0}^{\pi} d\theta \int\limits_{0}^{2\pi} d\varphi \frac{1}{(2\pi m_0 kT)^{3/2}} \exp\left(-\frac{p^2}{2m_0 kT}\right) p^2 \sin\theta$$

or

$$dW = \int\limits_{0}^{2\pi} d\varphi \int\limits_{0}^{\pi} \sin\theta \, d\theta \int\limits_{p}^{p+dp} \frac{p^2}{(2\pi m_0 kT)^{3/2}} \exp\left(-\frac{p^2}{2m_0 kT}\right) dp$$

The first integral equals 2π, and the second, $+2$. The last integral when the upper limit is infinitely close to the lower one equals the product of the integrand and dp. We again arrive at (3.31).

We can pass over from the momentum magnitude distribution (3.31) to an **energy distribution**. A particle of an ideal gas has only kinetic energy that equals $\varepsilon = p^2/(2m_0)$. Expressing the momentum in terms of the energy in (3.31), we obtain

$$dW = w_p \, dp = w_\varepsilon \, d\varepsilon = \frac{2}{\sqrt{\pi}} \frac{1}{(kT)^{3/2}} \exp\left(-\frac{\varepsilon}{kT}\right) \sqrt{\varepsilon} \, d\varepsilon$$

where it is taken into account that since $p = \sqrt{2m_0\varepsilon}$, we have

$$dp = \sqrt{\frac{m_0}{2}} \frac{d\varepsilon}{\sqrt{\varepsilon}}$$

Hence, *the probability of the energy of a particle being confined within the interval of values from* ε *to* $\varepsilon + d\varepsilon$ *is determined by the relation*

$$w_\varepsilon \, d\varepsilon = \frac{2\sqrt{\varepsilon}}{\sqrt{\pi}\,(kT)^{3/2}} \exp\left(-\frac{\varepsilon}{kT}\right) d\varepsilon \qquad (3.32)$$

Let us consider in greater detail the probability density for the **magnitude of the momentum**. Since the latter is a positive quantity, w_p has a meaning only for positive values of the argument. A plot of this function is shown in Fig. 3.5. When $p = 0$, we obtain $w_p = 0$, and for low values of p, when the exponential is virtually equal to unity, the probability density is proportional to the square of the momentum, so that the initial portion of the graph is a parabola. At large values of the momentum $(p \gg \sqrt{2m_0kT})$, w_p
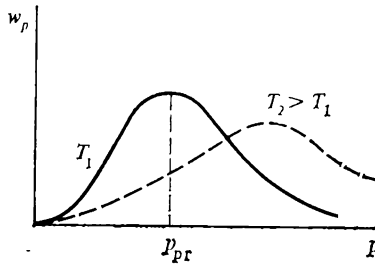
Fig. 3.5

rapidly diminishes owing to the exponential factor. It is not difficult to find the value of the momentum at which a maximum is reached. Differentiating the probability density with respect to p and equating the derivative to zero, we obtain an equation that determines, as is customarily said, the **most probable** value of the momentum:

$$\frac{dw_p}{dp} = \frac{4\pi}{(2\pi m_0 kT)^{3/2}} \left[2p \exp\left(-\frac{p^2}{2m_0 kT} \right) \right. $$
$$\left. - \frac{p^3}{m_0 kT} \exp\left(-\frac{p^2}{2m_0 kT} \right) \right] = 0$$

Hence, the most probable value of the momentum is

$$p_{pr} = \sqrt{2m_0 kT} \tag{3.33}$$

We obtain the following expression for the probability density at the maximum:

$$w_p(p_{pr}) = \frac{4}{\sqrt{\pi e}\, p_{pr}} = \frac{0.59}{\sqrt{m_0 kT}} \tag{3.34}$$

i.e. the maximum value of the probability density is inversely proportional to a square root of the temperature. If a gas is heated to a higher temperature T', the probability density changes (Fig. 3.5, the dashed line). The peak is displaced to the right and is somewhat lower; the curve is wider.

The probability density (3.31) helps us to find the mean values of functions of the value of the momentum. Let us find, for instance, the mean value of the magnitude of the momentum. According to the general rule, we have

$$\langle p \rangle = \int_0^\infty p w_p \, \mathrm{d} p = \int_0^\infty \frac{4\pi p^3}{(2\pi m_0 kT)^{3/2}} \exp\left(-\frac{p^2}{2m_0 kT}\right) \mathrm{d} p$$

If we introduce a new integration variable $x = p^2/(2m_0 kT)$, we have

$$\langle p \rangle = \frac{2}{\sqrt{\pi}} \sqrt{2m_0 kT} \int_0^\infty x \mathrm{e}^{-x} \, \mathrm{d} x$$

Since the integral over x equals unity*, we finally obtain

$$\langle p \rangle = \sqrt{\frac{8m_0 kT}{\pi}} \tag{3.35}$$

or for the mean value of the velocity

$$\langle v \rangle = \sqrt{\frac{8kT}{\pi m_0}} \tag{3.36}$$

For the mean value of the square of the momentum, we must write

$$\langle p^2 \rangle = \int_0^\infty p^2 \, \frac{4\pi p^2}{(2\pi m_0 kT)^{3/2}} \exp\left(-\frac{p^2}{2m_0 kT}\right) \mathrm{d} p$$

If we write this integral in the form

$$\langle p^2 \rangle = \frac{4\pi}{(2\pi m_0 kT)^{3/2}} \int_0^\infty p^4 \exp\left(-\frac{p^2}{2m_0 kT}\right) \mathrm{d} p$$

---

* $\displaystyle \int_0^\infty x \mathrm{e}^{-x}\, \mathrm{d} x = -\int_0^\infty x\, \mathrm{d}\,(\mathrm{e}^{-x}) = -x\mathrm{e}^{-x}\Big|_0^\infty + \int_0^\infty \mathrm{e}^{-x}\, \mathrm{d} x = 0 + (-\mathrm{e}^{-x})\Big|_0^\infty = 1$

then, comparing it with formula (A.13) given in Appendix 2 and taking into account that the integrand is even so that the integral from 0 to ∞ equals half the integral from $-\infty$ to $+\infty$, we can write

$$\langle p^2 \rangle = \frac{4\pi}{(2\pi m_0 kT)^{3/2}} \frac{3}{8} \sqrt{\pi} \, (2m_0 kT)^{5/2} = 3m_0 kT \quad (3.37)$$

It is even simpler to obtain this result as follows. Since

$$\langle p^2 \rangle = \langle p_x^2 \rangle + \langle p_y^2 \rangle + \langle p_z^2 \rangle$$

then, by using relation (3.22) by which $\langle p_x^2 \rangle = m_0 kT$ and similar ones for $\langle p_y^2 \rangle$ and $\langle p_z^2 \rangle$, we arrive directly at (3.37).

A comparison of (3.33), (3.35), and (3.37) shows that we may speak of three characteristic mean values of the momentum and of the values of the velocity corresponding to them:

the most probable value

$$p_{\mathrm{pr}} = \sqrt{2m_0 kT} \approx 1.41 \sqrt{m_0 kT}, \quad v_{\mathrm{pr}} \approx 1.41 \sqrt{\frac{kT}{m_0}}$$

the mean value

$$p_{\mathrm{m}} = \langle p \rangle = \sqrt{\frac{8m_0 kT}{\pi}} \approx 1.59 \sqrt{m_0 kT},$$

$$v_{\mathrm{m}} = \langle v \rangle \approx 1.59 \sqrt{\frac{kT}{m_0}}$$

and the root-mean-square value

$$p_{\mathrm{rms}} = \sqrt{\langle p^2 \rangle} = \sqrt{3m_0 kT} \approx 1.73 \sqrt{m_0 kT},$$

$$v_{\mathrm{rms}} \approx 1.73 \sqrt{\frac{kT}{m_0}}$$

It is convenient to use the probability density for the magnitude of the momentum in solving a very frequently encountered problem of finding the probability of the fact that the magnitude of a particle's momentum exceeds p_0 or, in other words, that the energy exceeds ε_0, where $\varepsilon_0 = p_0^2/(2m_0)$.

For example, for the proceeding of a reaction of nuclear fusion in which two nuclei of heavy hydrogen (deuterium) atoms combine to form a helium atom nucleus, the hydrogen atoms must have a sufficiently large energy. Indeed,

combination is possible only after the nuclei approach each other to a distance of the order of the size of a helium nucleus, i.e. to a distance of the order of 10^{-15} m. With account taken of the tunnel effect, approaching to a distance of 10^{-14} m is sufficient. Owing to the Coulomb forces of repulsion, such an approach is possible only for nuclei having a sufficiently high kinetic energy. Since the potential energy of two nuclei is

$$\varepsilon_p = \frac{e^2}{4\pi\varepsilon_0 r}$$

where e is the charge of a hydrogen atom nucleus (a positive charge equal to the charge of an electron), and $r \sim 10^{-14}$ m is the distance of closest approach, the initial kinetic energy that transforms into potential energy when the nuclei approach each other must be at least 2×10^{-14} J. If we determine the probability of a particle's energy exceeding this value, we can assess the intensity of the fusion reaction at a given temperature of the hydrogen plasma (see Problem 1 at the end of the chapter).

Another example can be taken from the field of the physics of a gas discharge. For a stable plasma to exist, the electrons in it must have an energy sufficient for ionization of the neutral atoms and their transformation into ions and new free electrons. This compensates for the loss of electrons due to their recombination. If the ionization energy is ε_i, we may have to determine the probability of an electron's energy being greater than ε_i (see Problem 2), or the momentum greater than $p_0 = \sqrt{2m_0\varepsilon_i}$.

The probability of the corresponding event is determined by the integral

$$W = \int_{p_0}^{\infty} w_p \, dp = \int_{p_0}^{\infty} \frac{4\pi p^2}{(2\pi m_0 kT)^{3/2}} \exp\left(-\frac{p^2}{2m_0 kT}\right) dp$$

If we introduce the variable $x = p/\sqrt{2m_0 kT}$, we have

$$W = \frac{4}{\sqrt{\pi}} \int_{p_0/\sqrt{2m_0 kT}}^{\infty} x^2 e^{-x^2} \, dx = -\frac{2}{\sqrt{\pi}} \int_{p_0/\sqrt{2m_0 kT}}^{\infty} x \, d(e^{-x^2})$$

Integration by parts yields

$$W = -\frac{2}{\sqrt{\pi}} \int\limits_{p_0/\sqrt{2m_0kT}}^{\infty} x \, d\,(e^{-x^2}) = -\frac{2}{\sqrt{\pi}} \, x e^{-x^2} \Big\lvert\limits_{p_0/\sqrt{2m_0kT}}^{\infty}$$

$$+\frac{2}{\sqrt{\pi}} \int\limits_{p_0/\sqrt{2m_0kT}}^{\infty} e^{-x^2}\,dx = \frac{2}{\sqrt{\pi}} \, \frac{p_0}{\sqrt{2m_0kT}} \exp\left(-\frac{p_0^2}{2m_0kT}\right)$$

$$+\left[1 - \mathrm{erf}\left(\frac{p_0}{\sqrt{2m_0kT}}\right)\right] \qquad (3.38)$$

where erf is the error function determined by relation (3.1). If the argument of the error function is much greater than unity (3 or more), only the first term may be retained, as follows from (3.4), i.e.

$$W \approx \frac{2}{\sqrt{\pi}} \, \frac{p_0}{\sqrt{2m_0kT}} \exp\left(-\frac{p_0^2}{2m_0kT}\right) \qquad (3.39)$$

3.8. Distribution Function

A knowledge of the Maxwell probability density allows us to find the mean number of particles having definite values of the momentum, velocity, or energy. Assume, for example, that we have chosen a volume element $d\tau$ in a vessel and we are interested in knowing the mean number of the molecules in it with momenta from the volume element $d\Omega$ in momentum space. If the concentration of the molecules is n, their mean number in the volume $d\tau$ is $n\,d\tau$. Since the probability of a molecule's momentum belonging to $d\Omega$ is $w_p\,d\Omega$, the mean number of molecules from the volume $d\tau$ having a given value of the momentum is obtained by multiplying their number by the relevant probability, i.e.

$$dN = n\,d\tau \cdot w_p\,d\Omega \qquad (3.40)$$

In statistics, *by a distribution function is customarily meant a function f such that, being multiplied by a volume element $d\tau$ in conventional space ($d\tau = dx\,dy\,dz$) and by a volume element $d\Omega$ in momentum space ($d\Omega = dp_x\,dp_y\,dp_z$) gives the mean number of particles in $d\tau$ and having the momentum from $d\Omega$,* i.e.

$$dN = f\,d\tau\,d\Omega \qquad (3.41)$$

A comparison of (3.40) and (3.41) shows that for an ideal gas in a vessel in the absence of external force fields, the distribution function equals the product of the concentration and the probability density of the values of the momenta: $f = nw_p$. Hence, for the Maxwell distribution, we have

$$\mathrm{d}N = f\,\mathrm{d}\tau\,\mathrm{d}\Omega = \frac{n}{(2\pi m_0 kT)^{3/2}}\exp\left(-\frac{p^2}{2\pi m_0 kT}\right)\mathrm{d}\tau\,\mathrm{d}\Omega \quad (3.42)$$

3.9. Particle Flux. Thermionic Emission

The solution of numerous practical and theoretical problems requires that we know how to evaluate what is called the **density of a particle flux.** We shall explain the meaning of this quantity. Consider a vessel containing an ideal
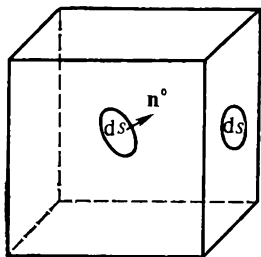
Fig. 3.6

gas. A small hole of area ds has been made in a side wall of the vessel (Fig. 3.6). The gas leaks out through the hole. The particle flux dJ is defined to be the number of particles crossing this area, i.e. flowing out of the vessel, in unit time. The flux density j is defined to be the ratio of the flux to the area, or the flux through a unit area: $j = \mathrm{d}J/\mathrm{d}s$.

It is naturally not compulsory to consider the flow of a gas out of a vessel. The magnitude of the flux may be related to an arbitrary elementary area ds mentally chosen inside the vessel. Such an area is shown in Fig. 3.6, and the vector $\mathbf{n}^0$ of unit length indicates the direction of a normal to this area. We usually speak of the vector of the elementary area ds, having in mind that the magnitude of this vector is ds, and its direction coincides with that of a normal to the area.

We first assume that instead of disordered chaotic motion, the particles of the ideal gas perform ordered motion at the

velocity **v** (with the momentum $\mathbf{p} = m_0\mathbf{v}$). Let us choose (Fig. 3.7a) an elementary area perpendicular to the direction of motion of the particles so that the vector d**s** will be parallel to **v** and calculate the flux dJ. During the time dt, the particles travel a path dl equal to v dt. Consequently, if we construct a right cylinder resting on the base ds and
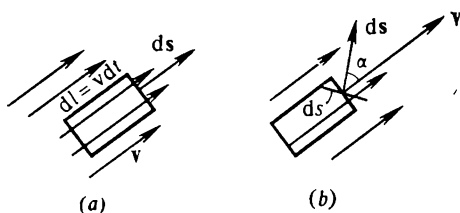
Fig. 3.7

having the altitude dl, during the time dt all the particles contained in it will cross the base. If n is the concentration of the particles in an infinitely small cylinder whose volume is

$$d\tau = d\mathbf{s} \cdot dl = d\mathbf{s} \cdot v \, dt$$

during the time dt, n dτ = nv ds dt particles will pass through the base. Hence, according to the definition of a flux, it follows that

$$dJ = \frac{n \, d\tau}{dt} = nv \, ds \qquad (3.43)$$

and for the flux density, that

$$j = \frac{dJ}{ds} = nv \qquad (3.44)$$

Let us see how formulas (3.43) and (3.44) will change if a normal to the area does not coincide with the direction of motion of the particles. Figure 3.7b shows an area ds whose normal makes the angle α with the direction of the velocity **v**. The projection of the area onto a plane perpendicular to the direction of motion, as can be seen from Fig. 3.7b, is ds_n = d$s \cos \alpha$.

The same number of particles crosses ds and ds_n during the time dt. Hence, using the result obtained above, we can

write the following expression for the flux dJ through ds:

$$dJ = nv \, ds_n = nv \cos \alpha \, ds \qquad (3.45)$$

Equation (3.45) is written in the vector form as follows:

$$dJ = n\mathbf{v} \cdot \mathbf{ds} \qquad (3.46)$$

where it has been taken into account that the scalar (dot) product of the vectors $\mathbf{v}$ and $\mathbf{ds}$ is $\mathbf{v} \cdot \mathbf{ds} = v \, ds \cos \alpha$. Let us now introduce the concept of the **flux density vector** as of a vector whose magnitude equals the density of the particle flux, and whose direction coincides with that of their motion, i.e.

$$\mathbf{j} = n\mathbf{v} \qquad (3.47)$$

Now relation (3.46) can be written as follows:

$$dJ = \mathbf{j} \cdot \mathbf{ds} \qquad (3.48)$$

Formula (3.45), which directly follows from (3.47) and (3.48),

$$dJ = \mathbf{j} \cdot \mathbf{ds} = n\mathbf{v} \cdot \mathbf{ds} = nv \cos \alpha \, ds$$

can be interpreted in a somewhat different way than was done above. If we designate by j_n the projection of the flux onto the direction of a normal to the area ds, then since $j_n = j \cos \alpha = nv \cos \alpha$, we obtain

$$dJ = j_n \, ds = nv \cos \alpha \, ds = nv_n \, ds$$

where v_n is the projection of the particles' velocity onto a normal to ds. The quantity j_n is known as the normal component of a flux to the area ds.

Let us now go over to an ideal gas in which there are particles moving in all directions. The determination of the flux density can be reduced to the one we have just considered if we introduce the concept of the elementary flux density $d\mathbf{j}$. We shall deal only with particles of the gas whose momentum belongs to the element $d\Omega$ of the momentum space, i.e. with particles having virtually the same value of the momentum (velocity). The number of such particles in unit volume is expressed in terms of the distribution function as follows:

$$dN = f \, d\Omega = nw_{\mathbf{p}} \, d\Omega$$

Their flux density by (3.47) will thus be

$$d\mathbf{j} = (nw_\mathbf{p}\,d\Omega)\,\mathbf{v} = \frac{\mathbf{p}}{m_0}\,nw_\mathbf{p}\,d\Omega \qquad (3.49)$$

Hence, *the elementary flux density* $d\mathbf{j}$ *of particles having the momentum* $\mathbf{p}$ *is defined to be a vector whose direction coincides with* $\mathbf{p}$ *and whose magnitude equals the number of particles having a momentum from* $d\Omega$ *crossing in unit time a unit area perpendicular to the direction of their motion, i.e. a vector determined by formula* (3.49).

When the distribution by momenta is a Maxwell one, we obtain the following expression for the elementary flux density:

$$d\mathbf{j} = \frac{\mathbf{p}}{m_0}\,\frac{n}{(2\pi m_0 kT)^{3/2}}\,\exp\left(-\frac{p^2}{2m_0 kT}\right)d\Omega \qquad (3.50)$$

The flux of particles having a momentum from $d\Omega$ through an arbitrary area $d\mathbf{s}$, according to (3.48), is

$$d\mathbf{j}\,d\mathbf{s} = \frac{nw_\mathbf{p}\,d\Omega}{m_0}\,\mathbf{p}\,d\mathbf{s} = \frac{nw_\mathbf{p}\,d\Omega}{m_0}\,p_n\,ds$$

where p_n is the component of the momentum normal to the area.

Relation (3.50) allows us to calculate the flux density of particles in various specific cases. Consider, for example, an electron gas in a semiconductor. In a first approximation, we may take no account of the interaction of the electrons with one another and consider them to be an ideal gas that obeys a Maxwell distribution in the equilibrium state. The resultant density of the flux evidently equals the sum of the elementary flux densities (3.50) for all possible momentum values, i.e.

$$\mathbf{j} = \int d\mathbf{j} = \int nw_\mathbf{p}\,\frac{\mathbf{p}}{m_0}\,d\Omega \qquad (3.51)$$

where the integral is evaluated over the entire momentum space.

Let us choose an elementary area and direct the z-axis of a Cartesian coordinate system at right angles to this area. Assume that it has a unit area, when the z-component of the flux density numerically equals the number of particles crossing it in unit time. If the electron gas is in equilibrium,

so that the distribution by momenta is Maxwellian, we have

$$j_z = \frac{n}{m_0} \int\limits_{-\infty}^{+\infty} \int\limits_{-\infty}^{+\infty} \int\limits_{-\infty}^{+\infty} \frac{p_z}{(2\pi m_0 kT)^{3/2}} \exp\left(-\frac{p^2}{2m_0 kT}\right) dp_x \, dp_y \, dp_z$$

The result can be seen to equal zero because the integrand is odd with respect to p_z, i.e. the number of particles having a given momentum crossing the area from left to right equals the number of particles crossing it from right to left.

A different result is obtained if we are interested in the flux of electrons crossing the area from left to right, i.e. having a positive value of the z-component of the momentum. Integration is now performed only over the positive values of p_z and over all (positive and negative) values of p_x and p_y. Writing the expression for the flux density as

$$j_z = \frac{n}{m_0} \int\limits_{-\infty}^{+\infty} dp_x \int\limits_{-\infty}^{+\infty} dp_y \int\limits_{-\infty}^{+\infty} dp_z \frac{p_z}{(2\pi m_0 kT)^{3/2}}$$

$$\times \exp\left(-\frac{p_x^2 + p_y^2 + p_z^2}{2m_0 kT}\right)$$

$$= \frac{n}{m_0} \int\limits_{-\infty}^{+\infty} \frac{1}{(2\pi m_0 kT)^{1/2}} \exp\left(-\frac{p_x^2}{2m_0 kT}\right) dp_x \int\limits_{-\infty}^{+\infty} \frac{1}{(2\pi m_0 kT)^{1/2}}$$

$$\times \exp\left(-\frac{p_y^2}{2m_0 kT}\right) dp_y \int\limits_{0}^{\infty} \frac{p_z}{(2\pi m_0 kT)^{1/2}} \exp\left(-\frac{p_z^2}{2m_0 kT}\right) dp_z$$

and taking into account that the integrals with respect to p_y and p_x according to the normalization condition equal unity, we have

$$j_z = \frac{n}{m_0} \int\limits_{0}^{\infty} \frac{p_z}{(2\pi m_0 kT)^{1/2}} \exp\left(-\frac{p_z^2}{2m_0 kT}\right) dp_z$$

It is simple to evaluate the last integral if we introduce the variable $y = p_z^2/(2m_0 kT)$. Indeed,

$$j_z = \frac{n}{m_0} \frac{\sqrt{2m_0 kT}}{2\sqrt{\pi}} \int\limits_{0}^{\infty} e^{-y} dy = \frac{n}{4} \sqrt{\frac{8kT}{\pi m_0}} \qquad (3.52)$$

Recall that by (3.36) the root is the mean velocity of the electrons, so that we finally have

$$j_z = \frac{n v_{\mathrm{m}}}{4} \qquad (3.53)$$

We must note that formula (3.53), if we do not indicate the value of the mean velocity specifically, follows only from the property of isotropy of the distribution function. Indeed, we can write

$$j_z = \frac{n}{m_0} \langle p \cos \theta \rangle^+$$

where θ is the angle between the direction of the momentum and the z-axis, while the plus sign signifies that the value of the function in angular brackets equals p_z when the p_z's are positive and zero when they are negative. For an isotropic distribution function when all directions are equally probable regardless of the value of the magnitude of the momentum, we have

$$\langle p \cos \theta \rangle^+ = \langle p \rangle \langle \cos \theta \rangle^+$$

i.e. the mean value equals the product of the mean value of the magnitude of the momentum and the mean value of a function equal to $\cos \theta$ when the cosine is positive and to zero when it is negative. Since the total solid angle is 4π and

$$\int\limits_0^{2\pi} d\varphi \int\limits_0^{\pi/2} \cos \theta \sin \theta \, d\theta = -2\pi \int\limits_0^{\pi/2} \cos \theta \, d(\cos \theta) = \pi$$

we have $\langle \cos \theta \rangle^+ = \pi/(4\pi) = 1/4$ and, consequently,

$$j_z = \frac{n}{m_0} \frac{\langle p \rangle}{4} = \frac{n v_{\mathrm{m}}}{4}$$

If the distribution is Maxwellian, formula (3.36) holds for v_{m}, and we again obtain (3.52).

Let us now consider the phenomenon of **thermionic emission** which consists in electrons flying out from a metal (or when special cathodes are used—from a semiconductor) heated to a high temperature. This effect is explained qualitatively as follows: the metal (or semiconductor) always has a certain number of electrons with such a large kinetic energy

that they are capable of overcoming the forces retaining them inside the cathode. The basic characteristic of a cathode determining its thermionic emission is a quantity called the **work function**. The latter equals the work that has to be done to emit an electron from the cathode. Without stopping to see what the work function A is determined by, we may consider it to be known from experiments.

Assume that the z-axis is perpendicular to the flat surface of the cathode. For the emission of an electron from a flat cathode, only motion along the z-axis is of significance. It thus follows that only those electrons leave the cathode whose kinetic energy of motion along the z-axis, i.e. $p_z^2/(2m_0)$ is greater than the work function A. Hence, the electrons will be emitted through the area ds on the surface of the cathode that move in a direction towards the surface (the positive direction of the z-axis) and for which the momentum component p_z is greater than

$$p_{z0} = \sqrt{2m_0 A} \qquad (3.54)$$

We obtain the flux of these electrons by integration over the positive values of the momentum from p_{z0} to ∞, i.e.

$$dJ = ds \int_{p_{z0}}^{\infty} \frac{n}{(2\pi m_0 kT)^{1/2}} \exp\left(-\frac{p_z^2}{2m_0 kT}\right) \frac{p_z}{m_0} \, dp_z$$

The same substitution of the variable as in the preceding case yields the result

$$dJ = ds \frac{n}{4} \sqrt{\frac{8kT}{\pi m_0}} \int_{p_{z0}^2/(2m_0 kT)}^{\infty} e^{-y} \, dy$$

$$= ds \frac{n v_m}{4} \exp\left(-\frac{p_{z0}^2}{2m_0 kT}\right)$$

For the density of the electron flux from the cathode, i.e. for the flux from unit area, with a view to (3.54), we obtain

$$j_z = \frac{n v_m}{4} \exp\left(-\frac{A}{kT}\right) \qquad (3.55)$$

Formula (3.53) derived previously for the density of an electron flux not emerging from a cathode is a particular case of formula (3.55) when $A = 0$.

The electron flux density is related quite simply to the **electric current density**. Indeed, every electron has a charge of $-e$, and, consequently, when j electrons pass through unit area in unit time, this signifies that it is crossed by a charge of $-ej$. Therefore, the current through unit area (i.e. the current density) is determined by the relation

$$i = -ej$$

The current density should be considered as a vector that for negatively charged electrons is directed oppositely to their motion, i.e. oppositely to the direction of the flux density:

$$\mathbf{i} = -e\mathbf{j} \qquad (3.56)$$

From (3.56) and (3.55), we obtain an expression for the density of a thermionic emission current:

$$i_z = -\frac{env_m}{4} \exp\left(-\frac{A}{kT}\right) \qquad (3.57)$$

The last equation showing how the current of thermionic emission depends on the properties of the cathode (n is the concentration of the electrons, and A is the work function) and the temperature which it is heated to is called the **Richardson formula** [v_m is determined by formula (3.52)]. Along general lines, it gives a good description of the phenomenon of thermionic emission, although, strictly speaking, it is not quite accurate because it does not take the physical properties of the cathodes into account with sufficient detail. For metals, the deviations are mainly associated with the fact that the electrons in them obey not a Maxwell distribution by momenta, but another one, which will be treated in Chap. 10. The deviations which we have just mentioned, however, are of a secondary nature because the exponential factor describing the rapid change in the current of thermionic emission as a function of the temperature is the basic one.

In experimental verification of the Richardson formula, one must have in view that the work function depends not only on the properties of the cathode material, but also on the state of its surface. An increase in the temperature may result in a change in the work function, and if such an effect occurs, it hampers a comparison of the experimental data with formula (3.57).

3.10. Experimental Verification of Maxwell Distribution

The Maxwell distribution was verified experimentally by many investigators. Reference is made most often to the experiment set up by O. Stern (1920). A plan view of the experimental arrangement he used is shown schematically in Fig. 3.8. The entire arrangement is contained in an evacuated volume. A platinum filament coated with a layer of silver is placed at the centre. The filament is heated by a current up to a temperature at which the silver begins to
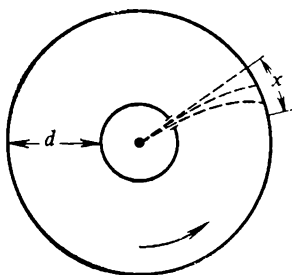
Fig. 3.8

evaporate and which is kept strictly constant in the following. Part of the evaporated atoms fly through the slot in the first cylinder surrounding the filament towards the second cylinder. If the cylinders are stationary, all the atoms that have passed through the slot are deposited on the second cooled cylinder forming a clear image of the slot. The two cylinders rotate in the experiment, however, and for this reason during the time in which a silver atom that has passed through the slot flies to the outer cylinder, the latter turns so that the atom is deposited at the point x not directly opposite the slot. The coordinate x depends on the flying time, i.e. on the velocity of the silver atom. If the momentum of an atom is p, the distance from the inner cylinder to the outer one is d, and the mass of the atom is m_0, the duration of the flight is $\Delta t = dm_0/p$. During this time, the outer cylinder will turn through the angle $\Delta\varphi = \omega\Delta t$, where ω is the angular velocity of rotation of the cylinders. The coordinate x is related to the angle of rotation $\Delta\varphi$ and the radius

R of the outer cylinder. If x is measured from a point oppo-
site the slot, we have $x = R\Delta\varphi$. Hence, a silver atom having
the momentum p gets to a point with the coordinate x,
where

$$x = R\Delta\varphi = R\omega\Delta t = \frac{R\omega\, dm_0}{p} \qquad (3.58)$$

If the evaporating atoms obey the Maxwell distribution,
the flux of atoms passing through the slot and having a
momentum ranging from p to $p + dp$ is determined by the
formula

$$J = C\,\frac{p^2}{(2\pi m_0 kT)^{3/2}}\,\exp\left(-\frac{p^2}{2m_0 kT}\right)\,dp \qquad (3.59)$$

that follows from (3.50) if we take into account the cylindri-
cal symmetry of the problem; C is a constant depending on
the parameters of the arrangement (the filament diameter,
the size of the slot, the distance from the filament to the slot,
etc.). Using (3.58) in going over from the values of the mo-
mentum p to the coordinate x, we obtain the following ex-
pression from (3.59) for the rate of deposition of the silver
atoms in the interval dx:

$$\frac{dN}{dt}\mid J\mid = C\,\frac{1}{(2\pi m_0\,kT)^{3/2}}\left(\frac{R\omega\,dm_0}{x}\right)^3\exp\left[-\frac{(R\omega\,dm_0/x)^2}{2m_0\,kT}\right]\frac{dx}{x} \qquad (3.60)$$

Formula (3.60) determines the distribution of the atoms
deposited on the outer cylinder if the width of the transmit-
ting slot Δ is very small, namely, it must be

$$\Delta^2 \ll \frac{(R\omega\,dm_0)^2}{2m_0\,kT} = \delta^2$$

Indeed, the parameter δ having the dimension of length
characterizes the shape of the distribution curve, and, par-
ticularly, it can be shown that the maximum of this curve
corresponds to $x = \delta/4$. If we assume for an assessment that
$R = 12$ cm, $d = 8$ cm, the number of revolutions a second
is equal to 400, and the temperature is about 1000 K, we
obtain $\delta \approx 6.6$ mm.
The results of the experiment within the accuracy limits
allowed by the arrangement agreed with the distribution
(3.60), i.e. confirmed the Maxwell distribution. The experi-
ment was repeated by a number of investigators in different

variants close in principle to Stern's experiment, with the use of other atoms, particularly bismuth, in addition to silver.

An example of another field in which the Maxwell distribution is established experimentally is probe measurements in the plasma of a gas discharge. **Plasma** is a gas in which a part of the atoms are ionized so that in addition to the neutral atoms (or molecules) there is a definite amount of electrons and positively charged ions. In the conventional conditions of existence of a gas-discharge plasma, when an electric current flows through it, it is a non-equilibrium system.
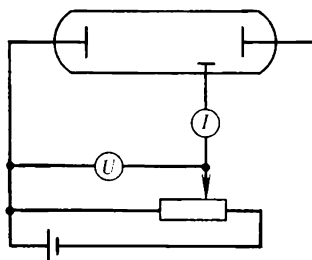
Fig. 3.9

The conditions are often such, however, that the distribution functions of the electrons and ions in the plasma, not mentioning the distribution function of the neutral atoms, are close to the Maxwell ones. The deviation of the distribution function from the equilibrium one will be treated in greater detail in Chap. 13.

Plasma is studied with the aid of probes—small electrodes placed in the region being studied. The probes are connected through a galvanometer and a controllable source of constant voltage (Fig. 3.9) to an electrode whose potential is assumed to be zero. By varying the voltage of the source, the dependence of the probe current registered by the galvanometer on the voltage U of the source, i.e. on the potential of the probe relative to the reference electrode, is measured.

If a probe is placed in plasma and its potential differs from that of the plasma in this region, a redistribution of the electrons and ions takes place. A cloud of a space charge is formed around the probe that screens it from the remaining plasma. Assume, for instance, that a probe has a negative

potential. It thus repels electrons and attracts positively charged ions so that a cloud of a positive charge is formed around it. The conditions in the plasma are distorted near a probe, but the plasma remains undisturbed where there is no space charge. The width of the region of a space charge depends on the electron and ion concentration, and at low pressures (less than 1 mmHg) it is usually so small that the electrons pass through this region without experiencing collisions. In these conditions, the current flowing to a probe is closely related to the flux of electrons and ions gaining the outer boundary of the space charge region. For a flat probe, the outer boundary of the space charge layer is approximately also flat and has about the same area s as the probe.

The probe characteristic, i.e. the dependence of the probe current on the potential applied, is especially simple at negative potentials of a probe relative to the region being investigated. In this case, the ions are attracted, and the electrons are repelled so that only those electrons get onto the probe whose kinetic energy is sufficient for surmounting the potential barrier:

$$A = -e (U - U_0) \qquad (3.61)$$

where U is the potential of the probe, and U_0 is the equilibrium potential of the plasma. What has been said signifies that the current of the electrons on a probe can be calculated by formula (3.57) in which the work function is assumed to equal the value given in (3.61):

$$J_e = is = se \, \frac{nv_{m, e}}{4} \exp \left[\frac{e (U - U_0)}{kT_e} \right]$$

Here n is the density of the electrons in the plasma, T_e is their temperature, $v_{m, e}$ is the mean velocity of the electrons. The ion current does not exceed the flow of ions to the outer boundary of the space charge region, i.e.

$$I_1 = es \, \frac{nv_{m, 1}}{4} \qquad (3.62)$$

Examination of Eq. (3.62) shows that at U's close to U_0 the ion current is less than the electron one because the mean velocity of the electrons $v_{m, e}$ is much higher than that of the ions. The ratio of these velocities at an identical tem-

perature of the electrons and ions equals the square root of
the ratio of their masses:

$$\frac{v_{m, e}}{v_{m, i}} = \sqrt{\frac{m_{0i}}{m_{0e}}}$$

At an atomic mass of an ion of the order of 20-50 amu, the
ion current is 1/50-1/60 of the electron current.

If we completely disregard the ion current, the probe
current will be

$$I \approx I_e = \frac{sen}{4} \sqrt{\frac{8kT_e}{\pi m_{0e}}} \, e^{e(U - U_0)/(kT_e)} \qquad (3.63)$$

In processing probe characteristics, it is customary prac-
tice to plot the logarithm of the probe current against the
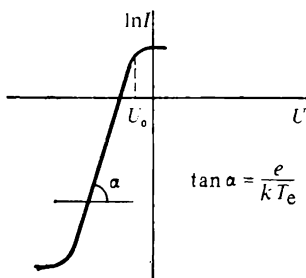
Fig. 3.10

probe potential. A typical plot of an experimentally obtained
relation is shown in Fig. 3.10. A glance at (3.63) shows that

$$\ln I = \frac{e}{kT_e} (U - U_0) + \ln \left(\frac{sen}{4} \sqrt{\frac{8kT_e}{\pi m_{0e}}} \right) \qquad (3.64)$$

Hence, the logarithm of the current is a linear function of
the potential, and the slope of the straight line is determined
by the temperature of the electrons ($\tan \alpha = e/kT_e$). As
the potential of the probe grows, the difference $U - U_0$
diminishes (recall that $U < U_0$). The potential barrier also
diminishes, and the electric current on the probe grows.
When the condition $U = U_0$ is reached, and the potential
continues to grow, the increase in the electron current be-
comes retarded because all the electrons getting onto the
outer boundary of the space charge region are attracted to

the probe. The increase in the current continues only owing to the growth in the effective area of the space charge region when U grows:

$$I_e = \frac{e n v_{m,e} s_{eff}}{4} \qquad (3.65)$$

Inspection of Fig. 3.10 shows how the bend in the probe characteristic can be used to find the plasma potential U_0. If we consider that at the point of bending s_{eff} for a flat probe equals the area of the probe s, Eq. (3.65) can be used to find the electron concentration. At very high negative potentials, the electron current on a probe becomes less than the ion one, i.e. the current on the probe changes its sign.

It is clear from the above that the presence of a straight section on the plot of the logarithm of the probe current against the probe potential points to a Maxwell velocity distribution of the electrons. The method of plotting probe characteristics is one of the widespread methods of investigating the plasma of a gas discharge. It was shown with the aid of probe characteristics that conditions may be realized in a discharge in which the electrons are distributed according to Maxwell's law, but with a temperature differing from that of the neutral atoms and ions. Such a plasma has been called **non-isothermal.** In processing experimental probe characteristics for non-isothermal plasma, the temperature T_e determined according to the slope of the probe characteristic is found to be higher than the temperature of the gas measured in other ways.

Hence, *the Maxwell distribution has been confirmed experimentally* (in experiments with molecular beams) *and has found great favour in a variety of applied problems* (in processing the probe characteristics of plasma, evaluating the current in semiconductor devices, etc.).

Exercises

1. *Assume that to sustain a continuous reaction of thermonuclear fusion (the combination of two deuterium nuclei into a helium nucleus), at least* $\gamma = 0.1\%$ *of all the deuterium nuclei must have an energy exceeding* $\mathscr{E}_0 = 10^4$ *eV. What is the temperature of the deuterium plasma at which a self-sustained reaction is possible?*
Solution. If the required temperature T satisfies the inequality $\mathscr{E}_0 \gg kT$, the probability of a deuterium nucleus having an energy

exceeding $\mathscr{E}_0$ is determined by formula (3.39), i.e.

$$\frac{\gamma}{100} = \frac{2}{\sqrt{\pi}} \cdot \frac{p_0}{\sqrt{2m_0\,kT}} \exp\left(-\frac{p_0^2}{2m_0\,kT}\right)$$

$$= \frac{2}{\sqrt{\pi}} \sqrt{\frac{\mathscr{E}_0}{kT}} \exp\left(-\frac{\mathscr{E}_0}{kT}\right)$$

Taking logarithms, we find

$$-\frac{\mathscr{E}_0}{kT} + \frac{1}{2}\ln\left(\frac{\mathscr{E}_0}{kT}\right) + \ln\left(\frac{2}{\sqrt{\pi}}\right) = \ln\left(\frac{\gamma}{100}\right)$$

that is

$$T = \frac{\mathscr{E}_0}{k\left[\frac{1}{2}\ln\left(\frac{\mathscr{E}_0}{kT}\right) + \ln\left(\frac{\mathscr{E}_0}{\sqrt{\pi}}\right) - \ln\left(\frac{\gamma}{100}\right)\right]}$$

This equation can be solved by successive approximations, assuming, for instance, in the zero approximation that $(3/2)\,kT_0 = \mathscr{E}_0$. In the first approximation

$$T_1 = \frac{\mathscr{E}_0}{k\left[\ln\left(\frac{2}{\sqrt{\pi}}\right) - \ln\left(\frac{\gamma}{100}\right) + \frac{1}{2}\ln\left(\frac{\mathscr{E}_0}{kT_0}\right)\right]}$$

in the second

$$T_2 = \frac{\mathscr{E}_0}{k\left[\ln\left(\frac{2}{\sqrt{\pi}}\right) - \ln\left(\frac{\gamma}{100}\right) + \frac{1}{2}\ln\left(\frac{\mathscr{E}_0}{kT_1}\right)\right]}$$

etc. For $\gamma = 0.1\%$, we have

$$T_0 = 7.7 \times 10^7 \text{ K}, \quad T_1 = 1.1 \times 10^7 \text{ K}, \quad T_2 = 0.9 \times 10^7 \text{ K}$$

Although the temperature T_0 does not satisfy the initial inequality, it does hold for T_2, so that the required temperature is $\sim T_2$.

2. *Measurements of the distribution function of electrons in a gas-discharge plasma in hydrogen showed that it is Maxwellian with an electron temperature of $T = 20\,000$ K. What fraction of the electrons is capable of ionizing neutral hydrogen atoms whose ionization energy $\mathscr{E}_1 = = 13.5$ eV?*

Solution. By the formula used in the preceding problem, we have

$$\frac{\gamma}{100} = \frac{2}{\sqrt{\pi}} \sqrt{\frac{\mathscr{E}_1}{kT}} \exp\left(-\frac{\mathscr{E}_1}{kT}\right)$$

Since $\mathscr{E}_1/kT \approx 8$, we have $\gamma \approx 0.1\%$.

3. *At what cathode temperature should one expect an appreciable ($i \approx \approx 1$ mA/cm^2) thermionic emission current from a tungsten ($A = = 4.5$ eV) and an oxide ($A = 1.8$ eV) cathodes? The concentration of the electrons in the metal is $n \approx 10^{22}\text{-}10^{23}$ cm^{-3}, and in the semiconductor is $n \approx 10^{18}\text{-}10^{19}$ cm^{-3}.*

Solution. We can use the Richardson formula for purposes of assessment both for semiconductors and for metals. After taking logarithms of this formula, we obtain

$$-\frac{A}{kT} + \ln\left(\frac{env_m}{4}\right) = \ln i, \quad \text{i.e.} \quad T \approx \frac{A}{k \ln\left(\dfrac{env_m}{4i}\right)}$$

Since $v_m = \sqrt{8kT/(\pi m_e)}$ depends on the temperature, we solve this equation by successive approximations:

$$T_0 = \frac{A}{k}, \quad T_1 = \frac{A}{k \ln\left(\dfrac{en}{4i}\sqrt{\dfrac{8A}{m_e\pi k}}\right)}$$

For tungsten, $T_1 \approx 1700$ K $\approx 1400\,°C$. For an oxide cathode, $T_1 \approx$ ≈ 1000 K $\approx 700\,°C$.

4. *Find the velocity of escape of the atmosphere and assess the time during which the atmosphere could leave the Earth. In solving the problem, assume that the Earth's atmosphere is a homogeneous layer with a certain effective thickness H_{eff}. It will be shown in the following chapter that the expression $H_{eff} = kT/(m_0 g)$ holds for H_{eff}. Assume in the calculations that $T = 300$ K, $g \approx 10$ m/s^2 (the acceleration of free fall), and $m_0 = 5 \times 10^{-26}$ kg is the mass of a molecule of nitrogen (oxygen).*

Solution. Since a molecule can leave the Earth when its velocity exceeds the escape velocity $v_0 = 11$ km/s, the density of the escape flux by (3.55) is

$$j = \frac{nv}{4} \exp\left(-\frac{mv_0^2}{2kT}\right)$$

Seeing that $v = \sqrt{\dfrac{8kT}{\pi m_0}} = 4 \times 10^2$ m/s, we have $j = e^{-730} \times$
$\times \dfrac{3 \times 10^{19} \times 4 \times 10^2}{4} = 3 \times 10^{-296}$ m^{-2}s^{-1}.

The total flux is

$$J = j4\pi R^2$$

where R is the Earth's radius. Since $J = -dN/dt$, where $N = 4\pi R^2 H_{eff} n$ is the total number of molecules in the atmosphere, we have

$$j = n\frac{v_m}{4}\exp\left(-\frac{m_0 v_0^2}{2kT}\right) = -H_{eff}\frac{dn}{dt}$$

that is

$$\tau = \frac{4H_{eff}}{v_m}\exp\left(\frac{m_0 v_0^2}{2kT}\right) = \frac{4kT}{m_0 g v_m}\exp\left(\frac{m_0 v_0}{2kT}\right)$$

has the meaning of the time characterizing the duration of existence of the atmosphere. Indeed, the preceding equation for the concentration can be written as $dn/dt = -n/\tau$. Its solution has the form $n = Ce^{-t/\tau}$. Substitution of the numerical values yields

$$\tau = 10^{319} \text{ s}$$

Chapter 4

BOLTZMANN DISTRIBUTION

4.1. Non-Uniformity of Particle Distribution in Space in the Presence of Force Fields

Up to now, we have considered the behaviour of an ideal gas not experiencing the action of external force fields. Not all the results we have obtained hold when such fields are present. *It is well known from experiments that upon the action of external forces, the uniform distribution of particles in space may be violated.* This is not surprising because, for example, under the action of the force of gravity, the molecules tend to settle to the bottom of the vessel or space confining them. Intensive thermal motion prevents this settling, and the molecules are distributed so that their concentration gradually diminishes with increasing height.

The task of this chapter is to reveal the law of distribution of particles in space when external force fields are present. Although in the case being considered, we could expect violation of the Maxwell distribution by momenta because the condition of isotropy of space used in deriving it is not observed, the Maxwell distribution actually remains in force.

It is expedient to begin our treatment of the nature of molecule distribution in space with graphs showing how the potential energy of a molecule depends on its position. Since in practice, it is convenient to plot such a graph only with one of the coordinates changing, we assume that the other two retain a constant value at this time. For instance, the potential energy of a molecule in the field of the gravitational force near the Earth's surface is determined by the equation

$$\varepsilon_{\mathrm{p}} = m_0 g z$$

where g is the acceleration of free fall, and z is the altitude. The corresponding plot (Fig. 4.1) has the form of a straight line. A similar graph can be constructed for any other force field having potential energy.

If an ideal gas is in a closed vessel from which the molecules cannot escape, the dependence of the potential energy
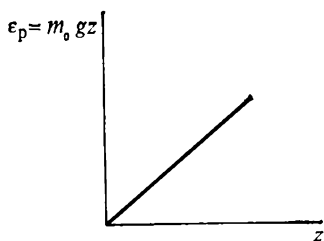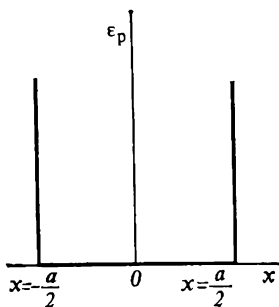
Fig. 4.1   Fig. 4.2

on the coordinate in the absence of external forces is shown graphically in Fig. 4.2. The points $x = -a/2$ and $x = +a/2$ correspond to the walls of the vessel. Within the vessel, i.e. when $(a/2) > x > (-a/2)$, the potential energy of the molecules is zero, and outside the vessel, i.e. when $|x| > a/2$, it is infinite, which corresponds to the infinitely great work that must be done to extract a molecule from the vessel through a wall. A graph of the type shown in Fig. 4.2 is known as a **potential well**.

Now assume that we have two vessels separated by a wall with an opening. We presume that within the limits of the opening there are forces that prevent the molecules entering the vessel *2* from the vessel *1* and facilitate their migration in the opposite direction. If the work A has to be done to overcome these forces and transfer a molecule from the first vessel to the second one, the magnitude of the potential energy in *2* is higher than in *1* by the amount $\Delta \varepsilon_p = A$. The plot of the potential energy has the form of a potential well with a stepped bottom (Fig. 4.3; it is assumed that the x-axis has been taken perpendicular to the wall and passes **through the opening**).

In each of the two vessels there occurs Maxwell distribution of the molecules by momenta corresponding to a certain
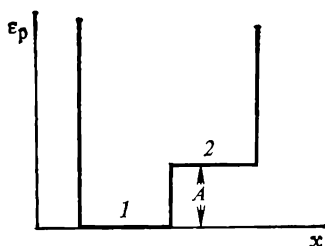
Fig. 4.3

temperature and concentration. Since the vessels communicate, the molecules from the first vessel can penetrate through the opening into the second one and, conversely, from the second vessel into the first one.

4.2. Detailed Balancing Principle

In the example considered in the preceding section, the equilibrium state is characterized by the fact that the migration of molecules from one of the communicating vessels into the second one is compensated by the opposite process of their migration from the second vessel into the first one. In other words, the equilibrium is of a dynamic nature, of the nature of a permanent exchange of molecules.

According to an example proposed by Ya. Frenkel, this exchange can be compared with the situation existing between two cities, for example, between Moscow and Leningrad owing to the constant moving of Leningrad inhabitants to Moscow and of Moscow inhabitants to Leningrad. It is obvious that we can speak of equilibrium of the population in these two cities only if the mean number of persons moving from Moscow to Leningrad is balanced by the mean number moving from Leningrad to Moscow. Moreover, the condition must be stated in greater detail. We can hardly speak of equilibrium if only women leave Leningrad and only men leave Moscow. Even with equal numbers of men and women moving in both directions, the conditions can-

not nevertheless be acknowledged as balanced if only young women move from Moscow and only old ones from Leningrad. It must be required that the age groups in both flows be the same on an average.

We have thus arrived at the **detailed balancing principle** that consists in the following. *In true equilibrium, with each flux there can be associated its opposite one so that equilibrium occurs not only as a whole, but also in detail for each pair of opposite processes.*

As applied to the communicating vessels considered above, the detailed balancing principle allows us to assert that in equilibrium the number of molecules with an energy value from a certain interval dε migrating from the first vessel to the second one equals on an average the number of molecules migrating in the opposite direction from the second vessel to the first one and after their migration having an energy value from the same interval dε. This situation allows us to solve the problem of the distribution of particles in space when external forces are present proceeding from the Maxwell distribution.

4.3. Relation Between Boltzmann and Maxwell Distributions

Assume that the opening in the wall separating two vessels has an area of ds and that the x-axis is perpendicular to the wall. By (3.50), the number of molecules from the momentum interval $d\Omega$ migrating from the first vessel to the second one in unit time is

$$ds\,dj_x = \frac{p_x n_1}{m_0\,(2\pi m_0\,kT_1)^{3/2}}\exp\left(-\frac{p^2}{2m_0\,kT_1}\right)\,d\Omega\,ds \qquad (4.1)$$

where n_1 is the concentration of the molecules in the first vessel, T_1 is their temperature, and p_x is the component of the momentum perpendicular to the plane of the opening. It is naturally assumed that the component of the momentum is, first, directed from the vessel *1* into *2* and, second, it is large enough for a molecule to surmount the potential barrier on its path. Since when a molecule passes through the opening it experiences a force acting in the direction of negative x's, the momentum component p_x diminishes, while the components p_y and p_z do not change. If we desig-

nate the value of the x-component of the momentum after passing through the opening by p'_x, by the law of energy conservation we must have

$$\frac{p_x^2}{2m_0} = \Delta\varepsilon_\mathrm{p} + \frac{(p'_x)^2}{2m_0} \tag{4.2}$$

i.e. the kinetic energy after migration becomes smaller because the potential energy grows.

According to the detailed balancing principle, the forward flux must be compensated by the reverse one, for which we can write, similarly to (4.1):

$$\mathrm{d}s\,\mathrm{d}j'_x = \frac{p'_x n_2}{m_0\,(2\pi m_0\,kT_2)^{3/2}} \exp\left[-\frac{(p')^2}{2m_0\,kT_2}\right]\mathrm{d}\Omega'\,\mathrm{d}s \tag{4.3}$$

Here n_2 and T_2 are the concentration and temperature of the molecules in the second vessel, and p' is their momentum. The latter is chosen in accordance with Eq. (4.2) so that after the migration of a molecule from one vessel into the other one its energy retains its value. Although the direction of the elementary flux density $\mathrm{d}j'_x$ is opposite to $\mathrm{d}j_x$ (negative x's), for migrations from 2 into 1 the direction of a normal to the area $\mathrm{d}s$ is also opposite, so that the flux directed into the first vessel is all the same positive.

It follows from the equality of the fluxes that

$$\frac{n_1 p_x}{m_0\,(2\pi m_0\,kT_1)^{3/2}} \exp\left(-\frac{p^2}{2m_0\,kT_1}\right)\mathrm{d}p_x\,\mathrm{d}p_y\,\mathrm{d}p_z$$
$$= \frac{n_2 p'_x}{m_0\,(2\pi m_0\,kT_2)^{3/2}} \exp\left(-\frac{p'^2}{2m_0\,kT_1}\right)\mathrm{d}p'_x\,\mathrm{d}p'_y\,\mathrm{d}p'_z \tag{4.4}$$

In a migration, the value of the components p_y and p_z does not change, therefore all the molecules for which the y-component of the momentum was within the interval $\mathrm{d}p_y$ will be in the interval $\mathrm{d}p'_y$, which equals $\mathrm{d}p_y$, after migration. The same holds for $\mathrm{d}p_z$. Hence,

$$\mathrm{d}p_y = \mathrm{d}p'_y,\ \ \mathrm{d}p_z = \mathrm{d}p'_z \tag{4.5}$$

With a view to (4.5), Eq. (4.4) can be rewritten as follows:

$$\frac{n_1}{(2\pi m_0\,kT_1)^{3/2}} \exp\left(-\frac{p^2}{2m_0\,kT_1}\right)\mathrm{d}\left(\frac{p_x^2}{2m_0}\right)$$
$$= \frac{n_2}{(2\pi m_0\,kT_2)^{3/2}} \exp\left(-\frac{p'^2}{2m_0\,kT_2}\right)\mathrm{d}\left(\frac{p'^2_x}{2m_0}\right) \tag{4.6}$$

It follows from the law of energy conservation (4.2) that

$$\mathrm{d}\left(\frac{p_x^2}{2m_0}\right) = \mathrm{d}\left(\frac{p_x'^2}{2m_0}\right)$$

because the change in the potential energy $\Delta\varepsilon_p$ in a migration from one vessel into the other one is the same for molecules with any momentum value. This allows us to represent the condition (4.6) in the form

$$\frac{n_1}{(2\pi m_0\, kT_1)^{3/2}}\, \exp\left(-\frac{p_x^2+p_y^2+p_z^2}{2m_0\, kT_1}\right)$$
$$=\frac{n_2}{(2\pi m_0\, kT_2)^{3/2}}\, \exp\left(-\frac{p_x'^2+p_y'^2+p_z'^2}{2m_0\, kT_2}\right)$$

or, since $p_y^2 = p_y'^2$ and $p_z^2 = p_z'^2$, in the form

$$\frac{n_1}{(2\pi m_0\, kT_1)^{3/2}}\, \exp\left(-\frac{p_x^2+p_y^2+p_z^2}{2m_0\, kT_1}\right)$$
$$=\frac{n_2}{(2\pi m_0\, kT_2)^{3/2}}\, \exp\left(-\frac{p_x'^2+p_y^2+p_z^2}{2m_0\, kT_2}\right)$$

Introducing into the right-hand side of the last equation the value of the kinetic energy $p_x'^2/(2m_0)$ from relation (4.2), we find

$$\frac{n_1}{(2\pi m_0\, kT_1)^{3/2}}\, \exp\left(-\frac{p_x^2+p_y^2+p_z^2}{2m_0\, kT_1}\right)$$
$$=\frac{n_2}{(2\pi m_0\, kT_2)^{3/2}}\, \exp\left(-\frac{\Delta\varepsilon_p}{kT_2}\right) \exp\left(-\frac{p_x^2+p_y^2+p_z^2}{2m_0\, kT_2}\right) \qquad (4.7)$$

Equation (4.7) must hold not at one definite value of the momentum, but must be an identity at any values. But in this case it can be satisfied only if the temperatures in the first vessel (T_1) and in the second one (T_2) are equal because only in this case do the exponential factors with p^2 cancel. After cancelling, we have

$$n_1 = n_2 \exp\left(-\frac{\Delta\varepsilon_p}{kT}\right) \qquad (4.8)$$

where $T = T_1 = T_2$ is the common temperature in both vessels.

The distribution (4.8) relating the concentrations of the molecules in the two vessels is known as the **Boltzmann distribution**. It holds for any potential force fields, and not

only for the particular example that was considered in deriving it. To show this, we can reason as follows. Assume that in the motion of a particle along a certain direction, for example, the x-axis, the potential energy changes in an intricate way (Fig. 4.4). The smooth nature of the change in the potential energy $\varepsilon_p(x)$ can be approximated to within
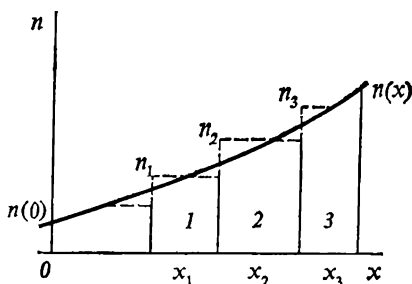
Fig. 4.4

any degree of accuracy by the stepped dashed line in Fig. 4.4 if the steps are reduced to a sufficiently small size. Let us consider the steps numbered 1, 2, and 3 corresponding to the positions x_1, x_2, and x_3 of a particle. Any two adjacent steps are covered by the above model, and we can therefore state that the temperature of the gas within the limits of any of them is the same, while the concentrations n_1, n_2, and n_3 are related by the expressions

$$n_2 = n_1 \exp\left(-\frac{\Delta\varepsilon_{p21}}{kT}\right), \quad n_3 = n_2 \exp\left(-\frac{\Delta\varepsilon_{p32}}{kT}\right) \quad (4.9)$$

where

$$\Delta\varepsilon_{p21} = \varepsilon_p(x_2) - \varepsilon_p(x_1) \text{ and } \Delta\varepsilon_{p32} = \varepsilon_p(x_3) - \varepsilon_p(x_2)$$

$$(4.10)$$

are the differences of the potential energies in migrating from one step to another. Let us introduce into the second of Eqs. (4.9) the value of n_2 from the first one. This yields

$$n_3 = n_1 \exp\left(-\frac{\Delta\varepsilon_{p21}}{kT}\right)\exp\left(-\frac{\Delta\varepsilon_{p32}}{kT}\right)$$

$$= p_1 \exp\left[-\frac{(\Delta\varepsilon_{p21}+\Delta\varepsilon_{p32})}{kT}\right]$$

But by (4.10), we have

$$\Delta\varepsilon_{p21} + \Delta\varepsilon_{p32} = \varepsilon_p(x_2) - \varepsilon_p(x_1) + \varepsilon_p(x_3) - \varepsilon_p(x_2)$$
$$= \varepsilon_p(x_3) - \varepsilon_p(x_1)$$

so that

$$n_3 = n_1 \exp\left[-\frac{\varepsilon_p(x_3) - \varepsilon_p(x_1)}{kT} \right] \qquad (4.11)$$

Hence, the Boltzmann distribution also holds for steps that are not direct neighbours and that do not exchange particles with each other. By considering a large number of steps, we can show that relations of the type of (4.11) hold for any two of them; for example,

$$n_5 = n_1 \exp\left[-\frac{\varepsilon_p(x_5) - \varepsilon_p(x_1)}{kT} \right], \text{ etc.}$$

If we take the step which the coordinate $x = 0$ corresponds to, and the step with the coordinate x, and if we designate the concentrations on these steps by $n(0)$ and $n(x)$, respectively, we obtain

$$n(x) = n(0) \exp\left[-\frac{\varepsilon_p(x) - \varepsilon_p(0)}{kT} \right] \qquad (4.12)$$

If, finally, we do not limit ourselves only to migrations along the x-axis, but assume that we are considering two arbitrary points in space with the position vectors $\mathbf{r} = \mathbf{r}_1$ and $\mathbf{r} = \mathbf{r}_2$, the Boltzmann distribution can be written in the following general form:

$$n(\mathbf{r}_2) = n(\mathbf{r}_1) \exp\left[-\frac{\varepsilon_p(\mathbf{r}_2) - \varepsilon_p(\mathbf{r}_1)}{kT} \right] \qquad (4.13)$$

Hence, *it follows from the detailed balancing principle and from the Maxwell distribution for momenta that in the presence of potential force fields it is essential for equilibrium that the temperature of the particles be the same everywhere and that the concentration change in accordance with relation (4.13) known as the Boltzmann distribution.*

4.4. Barometric Formula and Experimental Determination of the Boltzmann Constant

Using the Boltzmann distribution, we can easily obtain a barometric formula describing the change in the atmosphere's density with the altitude. If we assume the atmosphere

to be in equilibrium and, particularly, its temperature to be constant (this assumption is actually observed only approximately), the change in the concentration with the altitude is determined by formula (4.13). Let z stand for the altitude. Hence, the potential energy of a molecule of mass m_0 in the Earth's gravitational field is

$$\varepsilon_p(z) = m_0 g z$$

Designating the concentration at $z = 0$ by n_0, we can write the following formula for the concentration at the altitude z:

$$n(z) = n(0) \exp\left(-\frac{m_0 g z}{kT}\right) \qquad (4.14)$$

This expression is one of the possible forms of the barometric formula.

Since at constant temperature the pressure of a gas is proportional to its concentration, Eq. (4.14) is equivalent to the following form of the barometric formula:

$$p(z) = p_0 \exp\left(-\frac{m_0 g z}{kT}\right) \qquad (4.15)$$

where $p(z)$ is the pressure at the altitude z, and p_0 is the pressure at sea level ($z = 0$); $p_0 = 1$ atm $= 760$ mmHg $= 1.01 \times 10^5$ Pa.

It is sometimes convenient to write formulas (4.14) and (4.15) in a different way, expressing the Boltzmann constant k in terms of the molar gas constant R and Avogadro's constant N_A, i.e. $k = R/N_A$, and taking advantage of the fact that $m_0 N_A = \mu$, where μ is the molar mass. We thus obtain

$$n(z) = n(0) \exp\left(-\frac{\mu g z}{RT}\right) \qquad (4.16)$$

$$p(z) = p_0 \exp\left(-\frac{\mu g z}{RT}\right) \qquad (4.17)$$

Formulas (4.16) and (4.17) are more convenient in that they contain the molar mass instead of the mass of a molecule. We must note that since the Earth's atmosphere is mainly a mixture of two gases—nitrogen N_2 and oxygen O_2, the above formulas should be used for the concentration and the partial pressure of oxygen and nitrogen separately. The masses of the molecules N_2 and O_2 and their molar masses are close ($\mu = 0.028$ kg/mol for nitrogen and $\mu =$

= 0.032 kg/mol for oxygen). The difference is therefore often disregarded, and the molar mass of air is used ($\mu = 0.029$ kg/mol). According to Boltzmann's law, the composition of the atmosphere should change with the altitude in the direction of diminishing of its oxygen content and increasing its content of the lighter nitrogen.

Equation (4.14) can be written as

$$n(z) = n(0) \exp\left(-\frac{z}{H_{\text{eff}}}\right) \qquad (4.18)$$

where H_{eff} is the effective altitude:

$$H_{\text{eff}} = \frac{kT}{m_0 g} = \frac{RT}{\mu g} \qquad (4.19)$$

having the meaning of such an altitude at which the concentration of the molecules and, consequently, the pressure diminish to $1/e$ of their values at sea level.

At an unchanging density of the atmosphere equal to its density at sea level, the height of the atmosphere would be equal to H_{eff}. Indeed, when the barometric formula holds, the number of molecules above unit area of the Earth's surface at the altitude z in a layer having a thickness of dz is

$$dN = n(z)\,dz = n(0)\exp\left(-\frac{z}{H_{\text{eff}}}\right)dz$$

The total number of molecules above unit area is determined by summation over all the layers from those adjoining sea level to those at infinity, i.e.

$$N = \int dN = \int_0^\infty n(z)\,dz = n(0) \int_0^\infty \exp\left(-\frac{z}{H_{\text{eff}}}\right)\,dz$$
$$= n(0)H_{\text{eff}}$$

If the atmosphere were homogeneous, its height would be obtained by dividing N by $n(0)$, i.e. would be equal to H_{eff}.

As we have mentioned above, the barometric formula only approximately describes the change in pressure with altitude because the atmosphere is not actually in an equilibrium state. Nevertheless, this formula is very important since it allows us to carry out a number of useful assessments

and is the basis of other more accurate relations used in determining the altitude according to the pressure of the atmosphere.

J. Perrin proposed to use the barometric formula for the experimental determination of the numerical value of the Boltzmann constant. Since the latter is related to the molar gas constant known from experiments with rarefied gases, and to Avogadro's constant, the value of Avogadro's constant is also obtained from Perrin's experiment.

The idea underlying this remarkable experiment is very simple. The Boltzmann distribution and, consequently, the barometric formula, holds for any particles in thermal equilibrium with the surrounding medium. If we choose particles having a large mass in comparison with that of molecules, by formula (4.19) the effective altitude which is inversely proportional to the mass of the particles will be small. This provides great advantages in running an experiment. First, it is easier to measure the change in concentration if the latter varies over relatively small distances and not as in the atmosphere, where $H_{eff} \approx 9$ km. Second, it is simpler to ensure equilibrium conditions, particularly constancy of the temperature, because they are to hold in a relatively small region of space. In Perrin's experiment, a vessel with a liquid was filled with a powder of very fine particles. The latter may be treated as large molecules that under the action of the force of gravity are distributed in height non-uniformly in accordance with the barometric formula. A microscope is used to count the number of particles in the field of vision near the bottom of the vessel and then at a certain height from the bottom. Here advantage is taken of the microscope's property that only particles in a narrow zone near the focal plane can be seen in the field of vision. The ratio of the numbers obtained by the barometric formula is

$$\frac{n(z)}{n(0)} = \exp\left(-\frac{m'gz}{kT}\right) \tag{4.20}$$

where $m'g$ is the weight of a particle in the liquid, i.e. the weight less the Archimedean buoyant force. Inspection of formula (4.20) shows that

$$k = \frac{m'gz}{T} \ln\left[\frac{n(0)}{n(z)}\right] \tag{4.21}$$

If we know the size of the particles (their radius r) and the density ρ of the substance they consist of, and also the density ρ_0 of the liquid, we have

$$m'g = \frac{4}{3}\, \pi r^3 \left(\rho - \rho_0\right) g \qquad (4.22)$$

Knowing the temperature T of the liquid, one can determine k by (4.21) according to the experimentally found ratio $n\,(0)/n\,(z)$ for the chosen height z.

The value of $k = 1.38 \times 10^{-23}$ J/K has been obtained for the Boltzmann constant from Perrin's experiment. Hence, Avogadro's constant $N_A = 6.02 \times 10^{23}$ mol^{-1}.

4.5. Contact Potential Difference

We shall take the theory of the contact potential difference as another example of using the Boltzmann distribution. In the simplest variant of the classical (not quantum) theory of conductors, the latter are treated as unique vessels containing a gas of electrons. With greater accuracy, they should be considered as a positively charged ionic lattice between whose points electrons migrate, interacting with one another and with the lattice ions. As a whole, a crystal consisting of a positively charged lattice and electrons is neutral. The classical theory can be applied, for example, to semiconductors with a not too high concentration of mobile charge carriers.

To remove an electron from a conductor, it is necessary to spend a certain amount of work A known as the **work function** (more exactly, the **outer work function** or the **electron affinity**). The evaluation of the work function is a complicated task solved by the methods of quantum mechanics. Let us assume, as we did in considering the phenomenon of thermionic emission, that for a given specific conductor A is known from experiments.

The existence of the work function signifies that from the energy viewpoint, a conductor in a very simple model is a potential well. In Fig. 4.5, the energy of an electron is laid off along the axis of ordinates, and its coordinate x, along the axis of abscissas. If the conductor extends from a point with the coordinate $x = 0$ to a point with the coordinate $x = a$, the potential energy of an electron at these values

of x has one value, while at all other values of x it is greater by the magnitude of the work function A.

Let us now assume that we have two conductors *1* and *2*. Let n_1 and A_1 be the electron concentration in one of them
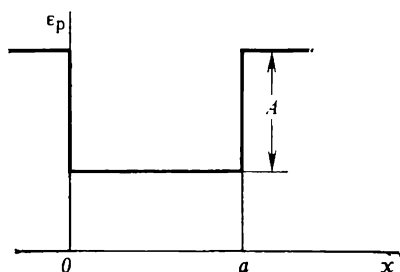
Fig. 4.5

and its work function, and n_2 and A_2—the relevant quantities for the other conductor. If these conductors are at such a great distance from each other that we may disregard
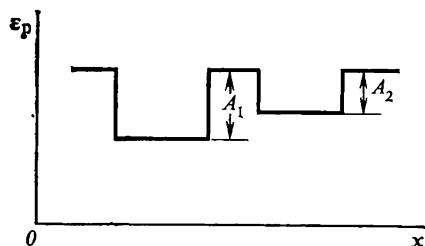
Fig. 4.6

the exchange of electrons between them, the energy diagram is as shown in Fig. 4.6. Indeed, the potential energy of an electron that has left a conductor and is outside it has the same value regardless of what conductor the electron has been removed from. In this connection, the top of the potential well corresponding to the level of the potential energy outside a conductor or to the level of a vacuum is the same for both conductors. The depth of the potential well, on the other hand, depends on the work function, and if

$A_1 > A_2$, the potential well corresponding to the first conductor is deeper, consequently, its bottom is lower (Fig. 4.6).

Matters are different if the conductors are so close to each other that the exchange of electrons has to be taken into account. Such an exchange exists in principle, even if only due to the effect of thermionic emission, in accordance with which an electron current flows from both conductors. What does the energy diagram look like in this case?

When the distance between the conductors is much smaller than the dimensions of the conductors themselves, they may be considered to have infinite dimensions along the surface of contact, i.e. along the y- and z-axes, and we may deal only with the dependence of the energy on the coordinate x normal to the surface of contact. Assume for definiteness that the concentration of the electrons in the first conductor (n_1) is lower than in the second one (n_2). Since the work function of the first conductor is higher and the concentration of the electrons here is lower than in the second conductor, it is natural that the current of thermionic emission from it is lower. This follows directly from formula (3.57) applied to the density of the current along the x-axis in the first and second conductors if we take into account that their temperature is the same and, consequently, the mean velocities v_m of the electrons are the same. The flow of electrons from the second conductor into the first one exceeds the opposite flow, and for this reason the first conductor begins to be charged negatively, and the second positively. What we call a **contact potential difference** appears between the conductors. The potential energy of an electron in the negatively charged conductor is higher than in the other one, and therefore for the charging process the first potential well in the energy diagram will be higher, and the second one will be lower. For the equilibrium state, the energy diagram acquires the form shown in Fig. 4.7. In this diagram, the tops of the potential wells are at different levels. The difference in the position is determined by the additional work that has to be done against the potential difference that appears when an electron migrates from the second conductor to the first one. If the electric potential of the first conductor is φ_1 and of the second is φ_2, then, since the

charge of an electron is $-e$, the additional work is

$$\Delta A = -e \, (\varphi_1 - \varphi_2) \qquad (4.23)$$

Applying the Boltzmann distribution law to the diagram in Fig. 4.7, we can express the contact potential difference $\varphi_1 - \varphi_2$ in terms of the work function and the concentration of the electrons for both conductors. It must be had in view here that the partial migration of electrons from the
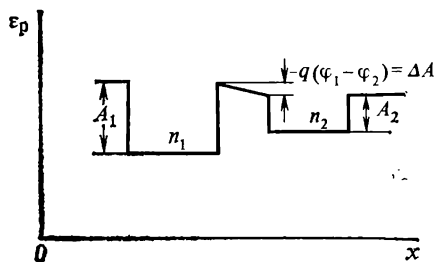
Fig. 4.7

second conductor to the first one does not virtually change the concentration because the number of electrons having migrated is very small in comparison with the total number of them in each of the conductors. In addition, the electric field of the contact potential difference is concentrated in a very narrow region near the contact. In this region, which we shall not consider here, the potential and the concentration of the electrons change from the values corresponding to one conductor to the values corresponding to the other one.

Inside the second conductor, the concentration, as before contact was established, is n_2, and inside the first one is n_1. A glance at the diagram shows that the difference of the potential energies of an electron in the first and second conductor is

$$\Delta \varepsilon_p = A_2 + \Delta A - A_1$$

According to Boltzmann's law,

$$\frac{n_1}{n_2} = \exp \left(-\frac{\Delta \varepsilon_p}{kT} \right) = \exp \left(-\frac{A_2 - A_1 + \Delta A}{kT} \right) \qquad (4.24)$$

Taking logarithms of Eq. (4.24) and introducing **the value** of ΔA from (4.23), we find

$$\ln \left(\frac{n_1}{n_2} \right) = - \frac{A_2 - A_1 - e\,(\varphi_1 - \varphi_2)}{kT}$$

whence for the contact potential difference we obtain

$$\varphi_1 - \varphi_2 = \frac{kT}{e} \ln \left(\frac{n_1}{n_2} \right) - \frac{A_1 - A_2}{e} \qquad (4.25)$$

It thus follows from the classical theory that *a contact potential difference sets in between two conductors whose value according to Boltzmann's law is determined by formula (4.25), i.e. depends on the work function and the concentration of electrons in both conductors.*

With an equilibrium contact potential difference, the current of the thermionic emission from one conductor to the other equals the reverse current in magnitude. This can be proved with no difficulty by direct calculations Eq. (4.25). Indeed, the density of the current from the first conductor to the second one by (3.57) is

$$i_{12} = \frac{en_1 v_m}{4} \exp \left(- \frac{A_1}{kT} \right) \qquad (4.26)$$

since although the contact potential difference helps the migration of electrons, this holds only with respect to electrons that have gotten into the contact field, i.e. that have already left the first conductor. The density of the reverse current is determined by the expression

$$i_{21} = \frac{en_2 v_m}{4} \exp \left(- \frac{A_2 + \Delta A}{kT} \right) \qquad (4.27)$$

because the electrons have to surmount not only the barrier A_2, but also the additional electrical barrier ΔA. If we substitute for n_1 in (4.26) its value from Eq. (4.24), we obtain

$$i_{12} = \frac{ev_m n_2}{4} \exp \left(- \frac{A_2 - A_1 + \Delta A}{kT} \right) \exp \left(- \frac{A_1}{kT} \right)$$

$$= \frac{ev_m n_2}{4} \exp \left(- \frac{A_2 + \Delta A}{kT} \right)$$

i.e. we see that $i_{12} = i_{21}$, as matters should be.

What is the value of the contact potential difference? The work function has values ranging from 0.5 to 4 eV, while

the electron concentration can change greatly. For example, in very pure silicon at room temperature, the concentration of the electrons has a value close to 10^{10} cm^{-3}. On the other hand, silicon is also used having a high electron concentration ranging from 10^{19} to 10^{20} cm^{-3}.

Assume that two semiconductors of a different chemical nature, but with an approximately equal electron concentration, are brought into contact. Now, calculating the contact potential difference by formula (4.25), we see that the main role is played by the second term. Since the work function has a value of the order of several electron-volts, the difference of work functions also has such a value. After division by the charge of an electron, we find that the contribution of the second term to the contact potential difference has a magnitude of the order of one or several volts. In the first term for room temperature ($T \approx 300$ K), we have $kT = 25 \times 10^{-3}$ eV, and, consequently, $kT/e = 25$ mV. If the concentration in contacting semiconductors differs by not more than one or two orders, the value of the factor $\ln (n_1/n_2)$ does not exceed 2.3 to 4.6. The first term is thus of the order of 100 mV, i.e. an order lower than the second term.

Matters are absolutely different in the contact of two pieces of a semiconductor having the same chemical nature, but with greatly differing electron concentrations, for example, two specimens of silicon with an electron concentration of 10^{10} and 10^{18} cm^{-3}. The work function is the same for both specimens, and for this reason the second term vanishes. The ratio of the electron concentrations is high (10^8), and therefore the logarithmic factor is not small:

$$\ln \frac{n_2}{n_1} = \ln (10^8) = 8 \ln 10 \approx 8 \times 2.3 \approx 18$$

Multiplying by $kT/e = 25$ mV, we obtain a contact potential difference equal to 0.45 V.

With the aid of formula (4.25), it is quite simple to obtain *Volta's law*, which states that *in a closed circuit consisting of several non-homogeneous semiconductors, the sum of the contact potential differences is zero.* Figure 4.8 shows a circuit consisting of three different conductors connected in series. For convenience in our further reasoning, we choose, say, a clockwise direction of circumvention of the cir-

cuit. Let φ_{12} be the contact potential difference at the boundary of the first and second conductors, φ_{23}—at the boundary of the second and third conductors, and φ_{31}—at the
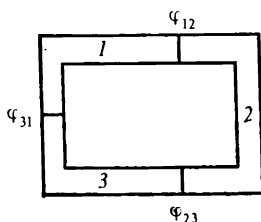
Fig. 4.8

boundary of the third and first ones. By (4.25), we have

$$\varphi_{12} = \frac{kT}{e} \ln \left(\frac{n_1}{n_2} \right) - \frac{A_1 - A_2}{e}, \qquad \varphi_{23} = \frac{kT}{e} \ln \left(\frac{n_2}{n_3} \right)$$
$$- \frac{A_2 - A_3}{e}$$

$$\varphi_{31} = \frac{kT}{e} \ln \left(\frac{n_3}{n_1} \right) - \frac{A_3 - A_1}{e} \qquad (4.28)$$

We obtain the sum of the contact potential differences in a closed circuit by summating Eqs. (4.28):

$$\varphi_{12} + \varphi_{23} + \varphi_{31} = \frac{kT}{e} \left[\ln \left(\frac{n_1}{n_2} \right) + \ln \left(\frac{n_2}{n_3} \right) + \ln \left(\frac{n_3}{n_1} \right) \right]$$
$$- \frac{1}{e} (A_1 - A_2 + A_2 - A_3 + A_3 - A_1)$$

It can be seen that the term containing the work functions vanishes. If the circuit is in equilibrium so that the temperature of all the conductors is the same, the sum of the remaining terms also vanishes:

$$\ln \left(\frac{n_1}{n_2} \right) + \ln \left(\frac{n_2}{n_3} \right) + \ln \left(\frac{n_2}{n_1} \right)$$
$$= \ln \left(\frac{n_1 n_2 n_3}{n_2 n_3 n_1} \right) = \ln 1 = 0$$

Hence, the sum of the contact potential differences does indeed equal zero, and it is evident that this holds for a circuit consisting of any number of non-homogeneous conductors.

4.6. Method of Self-Consistent Field

In some problems, the use of the Boltzmann formula is hindered by the fact that the potential energy determining the distribution of particles in space depends on their position. The distribution of charged particles (electrons and ions) in a gas discharge is a typical example of such a case. The same relates to the distribution of electrons in the contact layer of two conductors where, as we established in the preceding section, the contact potential difference depends on the electron concentration. Such a difficulty appears when, strictly speaking, one attempts to fall outside
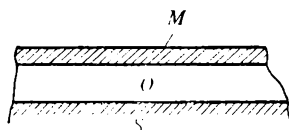
Fig. 4.9

the limits of applicability of the Boltzmann distribution law and, in addition to the influence of the external force fields for which the distribution was derived, takes into account the fields set up by the particles themselves, i.e. actually takes into account the forces of interaction between them. The method of taking into account the forces of interaction with the aid of the Boltzmann distribution that is set out in the present section is known as the **method of the self-consistent field**. It is applied most frequently to charged particles because the conditions in which it holds are observed the best for them.

To explain the essence of the method of the self-consistent field with greater clarity, it will be good to revert to a specific problem. In the M-O-S (metal-oxide-semiconductor) transistors that have come into favour, one of the electrodes called the gate is designed as follows. A thin layer of an oxide film O (Fig. 4.9) that is a good insulator is applied onto the semiconductor S. A metal electrode M is sprayed onto the film. The potential of the gate relative to the semiconductor can be varied with the aid of an external source; owing to the presence of the oxide film, virtually no current flows through the system. Assume, for example, that we

have to do with a semiconductor in which the concentra-
tion of the free electrons is n_1 (what is called an n-type semi-
conductor). The charge of the electrons in it is compensated
by the positive charge associated with the crystal lattice
and distributed uniformly. If for purposes of simplifying
our problem we do not consider the intricate phenomena
that may occur on the semiconductor-oxide interface and
that are due to the structure of this interface, we must
consider that the concentration of the electrons on the oxide-
semiconductor interface is the same as what there would be
on the metal-semiconductor interface in the absence of the
oxide film.

Assume that the work function of the metal is lower and
the electron concentration in it is higher than in the semicon-
ductor. In the absence of an external voltage, the semicon-
ductor contact layer becomes enriched with electrons and
is charged negatively, while the corresponding contact layer
of the metal is charged positively. It must be borne in mind
here that the change in the concentration of the electrons
in the contact layer occurs by exchange via the external
circuit, and not through the oxide layer.

Owing to the high concentration of the electrons in the
metal, the redistribution of the charge in it hardly affects
the concentration, therefore in the semiconductor on the
interface with the oxide film it may be considered equal to
the concentration n_2 of the electrons in the metal.

Hence, the semiconductor has a layer of a space charge,
and the concentration of the electrons in it smoothly changes
from the value that sets in on the interface to the value
inside the semiconductor. A potential difference preventing
the further redistribution of the electrons is formed at the
expense of the charge of this layer. If an external voltage U
is also applied between the gate and the semiconductor, the
layer of the space charge sets up such a potential difference
that is sufficient for compensating the sum $\varphi_c + U$—the
contact potential difference and the applied external vol-
tage. The polarity of the applied voltage is very important
because in the given example with a positive charge on the
metal and a negative one on the semiconductor, it is added
to the contact potential difference, and with the reverse
polarity it is subtracted.

Let us now determine the width of the region of the space

charge and the distribution of the electrons in it. Since no current flows through the system, the electrons acquire an equilibrium distribution, i.e. the latter is determined by the Boltzmann formula

$$n = n_1 \exp\left(\frac{e\varphi}{kT}\right) \qquad (4.29)$$

where n_1 is the concentration inside the semiconductor, the potential of this region being taken equal to zero. As we have already noted, formula (4.29) does not give a solution of the problem because the potential remains an unknown position function. To determine it, we must turn to the laws of electrostatics (the applied voltage is assumed to be constant or to vary sufficiently slowly). An equation relating the potential and the volume density ρ of a charge is derived in electrostatics. This equation, known as the **Poisson equation,** is

$$\nabla^2\varphi = -\frac{\rho}{\varepsilon\varepsilon_0} \qquad (4.30)$$

where ε is the permittivity of the semiconductor, ε_0 is the electric constant, and the symbol $\nabla^2\varphi$ has the following meaning:

$$\nabla^2\varphi = \frac{\partial^2\varphi}{\partial x^2} + \frac{\partial^2\varphi}{\partial y^2} + \frac{\partial^2\varphi}{\partial z^2} \qquad (4.31)$$

The charge density ρ is related to the electron concentration n and the positive charge of the lattice by the expression

$$\rho = -en + en_1 \qquad (4.32)$$

because $-en$ is the negative charge of the electrons per unit volume, and en_1 is the corresponding positive charge of the crystal lattice. The quantity n_1 is constant because the charge of the lattice is distributed in it uniformly and is not redistributed under the action of an external field.

By substituting for n in (4.32) its value from (4.29), we can obtain

$$\rho = -en_1\left[\exp\left(\frac{e\varphi}{kT}\right) - 1\right] \qquad (4.33)$$

With the aid of expression (4.33), the Poisson equation can be written as

$$\nabla^2\varphi = \frac{en_1}{\varepsilon\varepsilon_0}\left[\exp\left(\frac{e\varphi}{kT}\right) - 1\right] \qquad (4.34)$$

Hence, *if the potential of an electric field depends on electric charges whose distribution is determined by the field they set up, to find the potential we must solve an equation of a self-consistent field of the type of (4.34), and then with the aid of the found potential use Boltzmann's law to find the concentration of the mobile charged particles (electrons).*

Equation (4.34) does not include the external field, but its solution does depend on it. The matter is that for a single-valued solution in a certain region of space we must know the values of the potential or strength of the electric field on the boundary of this region, i.e. the **boundary conditions** must be set. If in the example being considered, an external source of an e.m.f. produces the potential difference U between the gate and the semiconductor, the boundary conditions can be taken in the following form. In the unperturbed (i.e. sufficiently far from the gate) part of the semiconductor, the potential equals zero, while in its part adjoining the oxide film the potential virtually coincides with the sum $\varphi_c + U$ (the oxide film is assumed to be sufficiently thin, and the potential difference across it may be ignored).

The equation of a self-consistent field is not linear (the required quantity is in the argument of the exponential function), and for this reason its solution involves difficulties that are surmounted, as a rule, by using computers. There are cases, however, when the equation is solved quite simply approximately. One of them is the case when the potential φ is small in comparison with the quantity kT/e. At room temperature, this condition is observed if the sum $\varphi_c + U < 25$ mV. In this case, taking advantage of the smallness of the argument, it is good practice to expand the exponential function into a series and retain the first two terms of the series, i.e. write

$$\exp\left(\frac{e\varphi}{kT}\right) \approx 1 + \frac{e\varphi}{kT}$$

Equation (4.34) becomes linear in this approximation:

$$\nabla^2\varphi = \frac{e^2 n_1}{\varepsilon\varepsilon_0 \, kT}\,\varphi \tag{4.35}$$

and can therefore be solved by methods known from mathematics.

To reveal some characteristic features of the phenomenon described by Eq. (4.35), we shall consider in greater detail the case when the problem is reduced to a single-dimensional one, i.e. when the gate and the semiconductor have an infinite flat surface. The distribution of the potential depends only on the single coordinate x perpendicular to the plane of contact. Equation (4.35) is written in the form

$$\frac{d^2\varphi}{dx^2} = \frac{e^2 n_1}{\varepsilon \varepsilon_0 \, kT} \, \varphi \qquad (4.36)$$

because the derivatives with respect to y and z vanish.

For our further treatment, it will be convenient to introduce the symbol

$$\delta = \sqrt{\frac{\varepsilon \varepsilon_0 \, kT}{e^2 n_1}} \qquad (4.37)$$

where the parameter δ has the dimension of length and is known as the **Debye length**. Using the Debye length, we can write Eq. (4.36) as follows:

$$\frac{d^2\varphi}{dx^2} = \frac{\varphi}{\delta^2} \qquad (4.38)$$

The general solution has the form

$$\varphi = C_1 e^{-x/\delta} + C_2 e^{x/\delta} \qquad (4.39)$$

where C_1 and C_2 are constants whose values are determined with the aid of the boundary conditions.

At a sufficiently remote distance from the gate ($x \to \infty$), the semiconductor is unperturbed, and the potential is zero. Since at $x \to \infty$ the first term in (4.39) tends to zero, and the second, to infinity, it is necessary to assume (the coordinate of the contact is $x = 0$) that

$$C = U + \varphi_c \text{ and } C_2 = 0$$

The solution of Eq. (4.39) satisfying the boundary conditions thus has the form

$$\varphi = (U + \varphi_c) \, e^{-x/\delta} \qquad (4.40)$$

It is characteristic that the potential exponentially diminishes with an increasing distance from the gate so that at a distance equal to the Debye length it diminishes to $1/e \approx 1/2.7$ of its initial value. A qualitatively similar

distribution is also encountered when the applied potential is not small in comparison with kT/e. Indeed, if we measure the potential in units of kT/e, that is, if we introduce the dimensionless potential $\psi = e\varphi/(kT)$, the equation of a self-consistent field is reduced to the form

$$\nabla^2\psi = \frac{e^2 n_1}{kT\,\varepsilon\varepsilon_0}\,(e^\psi - 1), \quad \text{or} \quad \nabla^2\psi = \frac{1}{\delta^2}\,(e^\psi - 1) \quad (4.41)$$

i.e. the Debye length is again a parameter characterizing the distribution of the potential. Although the law of the change in the potential is now different (it is not an exponential one), it is evident from physical considerations that in this case too screening by mobile charges occurs at a distance of the order of the Debye length.

In Sec. 3.10 when discussing probe characteristics, we indicated that the thickness of the space charge layer near a probe must be small for the electrons to pass through it without collisions. It can be seen from the above that the thickness of this layer has the order of the Debye length so that it can be readily assessed if we know the concentration of the charged particles and the temperature of the gas (see Example 3 to the present chapter).

We must note that the expression for the electron current flowing to a probe derived on an earlier page can be obtained by reasoning in a different way and using the Boltzmann distribution. In accordance with the latter, the concentration of the electrons directly near a probe is

$$n_0 = n \exp\left[\frac{e\,(U-U_0)}{kT}\right]$$

Those of them moving towards the probe will get onto it so that the current density is

$$|\,i\,| = ej = \frac{en_0 v_{\mathrm{m}}}{4} = \frac{ev_{\mathrm{m}}n}{4}\,\exp\left[\frac{e\,(U-U_0)}{kT}\right]$$

This example illustrates the close relation between the Maxwell and the Boltzmann distributions.

We must make some concluding remarks on the applicability of the method of a self-consistent field. Although Eq.

(4.41) may be used for much higher potentials than (4.36), we must have in view that a different restriction is imposed on its applicability. Using the concept of the charge density in the Poisson equation, we imply that either the volumes in which the potential still varies relatively slightly contain many charged particles or, if this condition is violated, we have to take the time-averaged value of the charge density.

In the first case, assessing the volume by quantity δ^3, we must write

$$n\delta^3 \gg 1$$

If we substitute into this expression the value of the Debye length from (4.37), we find that the equation may be applied when

$$n \ll \left(\frac{\varepsilon\varepsilon_0\,kT}{e^2} \right)^3 \tag{4.42}$$

For example, for room temperature ($T \approx 300$ K) in a semiconductor with $\varepsilon = 10$, this gives $n \ll 10^{15}$ cm^{-3}.

In the second case, when the condition (4.42) is violated, by φ and n we may understand time-averaged quantities. For weak fields by (4.33), we have

$$\rho = en_1 \left[1 - \exp\left(\frac{e\varphi}{kT} \right) \right] \approx -e^2 n_1 \frac{\varphi}{kT} \tag{4.43}$$

i.e. the charge density is linearly related to the potential and, consequently, the time-averaged concentration is determined in terms of the time-averaged potential by the same condition (4.43). Therefore, Eq. (4.36) may be considered correct for mean values of the potential. For strong fields, since the mean value of the exponential when the condition (4.42) is violated does not coincide with its value calculated for the mean potential, i.e.

$$\left\langle \exp\left(\frac{e\varphi}{kT} \right) \right\rangle \neq \exp\left(\frac{e\,\langle\varphi\rangle}{kT} \right)$$

we cannot use relation (4.33) so that Eq. (4.41) may not be used for evaluating the time-averaged potential.

Similar equations and conclusions can also be obtained for gases. A certain distinction is associated with both the negative (electrons) and positive (ions) charges being mobile in gases. We shall not stop to consider this, however.

Exercises

1. *The Earth's atmosphere at sea level consists of* 78% *nitrogen and* 22% *oxygen (by volume). What is the content of these gases in per cent at an altitude equal to the effective altitude of the atmosphere if the latter may be considered to be in equilibrium at a temperature of* $T = 300$ *K?*
Solution. The effective altitude of the atmosphere, with a molar mass of the air of $\mu_{air} = 0.029$ kg/mol, is, according to Eq. (4.19),

$$H_{eff} = \frac{RT}{\mu_{air}g} = \frac{8.3 \times 300 \times 10^3}{29 \times 9.81} \text{ m} = 8.75 \times 10^3 \text{ m} = 8.75 \text{ km}$$

The concentration at the altitude H_{eff} by (4.16) is

$$n_{O_2} = n_{O_2}(0) \, e^{-\mu_{O_2}gH_{eff}/(RT)}, \quad n_{N_2} = n_{N_2}(0) \, e^{-\mu_{N_2}gH_{eff}/(RT)}$$

Hence, the oxygen content in per cent is

$$p_{O_2} = 100 \frac{n_{O_2}}{n_{O_2} + n_{N_2}} = \frac{100 n_{O_2}(0)}{n_{O_2}(0) + n_{N_2}(0) \, e^{-(\mu_{N_2} - \mu_{O_2})gH_{eff}/(RT)}}$$

$$\approx \frac{100 n_{O_2}(0)}{n_{O_2}(0) + n_{N_2}(0)} \left(1 + \frac{n_{N_2}(0)}{n_{O_2}(0) + n_{N_2}(0)} \right.$$

$$\left. \times \frac{(\mu_{N_2} - \mu_{O_2}) gH_{eff}}{RT} \right) = 20\%$$

where the condition is used that

$$\frac{\mu_{O_2} - \mu_{N_2}}{RT} gH_{eff} = \frac{\mu_{O_2} - \mu_{N_2}}{\mu_{air}} \frac{\mu_{air}gH_{eff}}{RT} = \frac{\mu_{O_2} - \mu_{N_2}}{\mu_{air}} = \frac{4}{29} \ll 1$$

The nitrogen content in per cent is

$$p_{N_2} = 100 - p_{O_2} = 80\%$$

2. *In Perrin's experiment, particles having a density of* $\rho = 2.6$ g cm^{-3} *and a diameter of* $2r = 0.1$ μm *are used. They are suspended in water. What is the ratio between the concentration of the particles at the bottom and at a distance of* 1 mm *from the bottom at a temperature of* $T = 300$ K?
Solution. The effective mass of a particle is

$$m' = \frac{4}{3} \pi r^3 (\rho - \rho_0) = 8 \times 10^{-5} \text{ g}$$

The ratio of the concentrations is

$$\exp\left(\frac{m'gH}{kT} \right) = e^2 = 7.5$$

3. *The concentration of the electrons and ions in a plasma is* $n = 10^{12}$ cm^{-3}. *The temperature of the ions and neutral molecules is* 300 K. *Assess the order of magnitude of the space charge layer thickness near a probe.*

Solution. In its order of magnitude, the thickness of the space charge layer equals the Debye length. In the given case

$$\delta = \sqrt{\frac{\varepsilon\varepsilon_0\,kT}{e^2 n}} = \sqrt{\frac{\varepsilon_0\,kT}{e^2 n}} \approx 7 \;\mu m$$

(the permittivity $\varepsilon = 1$, the charge of an electron $-e = 1.6 \times 10^{-19}$ C, the constants $\varepsilon_0 = 8.85 \times 10^{-12}$ F/m, and $k = 1.38 \times 10^{-23}$ J/K).

Chapter 5

GIBBS DISTRIBUTION

5.1. Maxwell-Boltzmann Distribution Function

We established in Sec. 3.8 that in the absence of external fields, the distribution function f that determines the mean number dN of particles in the volume $d\Omega$ of momentum space and in the volume $d\tau$ of conventional space is given by expression (3.42), which we shall rewrite for convenience of reference:

$$dN = f\,d\tau\,d\Omega = \frac{n}{(2\pi m_0\,kT)^{3/2}}\exp\left(-\frac{p^2}{2m_0\,kT}\right)d\Omega\,d\tau \quad (5.1)$$

Let us now establish the appearance of the equilibrium distribution function *in the presence of force fields*. In this case, the particles are distributed in space non-uniformly, and the number of particles in the volume element $d\tau$ of space is

$$n\,(\mathbf{r})\,d\tau \qquad\qquad (5.2)$$

where $n\,(\mathbf{r})$ is the concentration. The momentum distribution remains Maxwellian as previously, so that the probability dW of the momentum of a particle being confined in $d\Omega$ is determined according to the last of Eqs. (3.21) by the formula

$$dW = \frac{1}{(2\pi m_0\,kT)^{3/2}}\exp\left(-\frac{p^2}{2m_0\,kT}\right)d\Omega \qquad (5.3)$$

The number of molecules dN in the volume $d\tau$ and having a momentum from $d\Omega$ can be found by multiplying (5.2) by the probability (5.3) of the corresponding value of the mo-

mentum, i.e.

$$dN = n(\mathbf{r})\, d\tau\, dW = \frac{n(\mathbf{r})}{(2\pi m_0 kT)^{3/2}} \exp\left(-\frac{p^2}{2m_0 kT}\right) d\tau\, d\Omega$$

(5.4)

The last expression differs from (5.1) only in that now the concentration is not a constant number, but varies from point to point. Since the dependence of the concentration on the coordinate for equilibrium is determined by the Boltzmann distribution (4.13), we can rewrite relation (5.4) in the form

$$dN = n(\mathbf{r}_1) \exp\left[\frac{\varepsilon_{\mathrm{p}}(\mathbf{r}_1)}{kT}\right] \frac{1}{(2\pi m_0 kT)^{3/2}} \exp\left[-\frac{\varepsilon_{\mathrm{p}}(\mathbf{r})}{kT}\right]$$
$$\times \exp\left(-\frac{p^2}{2m_0 kT}\right) d\tau\, d\Omega$$

(5.5)

where $n(\mathbf{r}_1)$ is the concentration of the molecules at a point $\mathbf{r}_1$, and $\varepsilon_{\mathrm{p}}(\mathbf{r}_1)$ is their potential energy at this point.

We obtain a different form of relation if we designate the factor not depending on the instantaneous coordinates $\mathbf{r}$ and the momentum $\mathbf{p}$ by C_N and combine the exponential factors:

$$dN = C_N \exp\left[-\frac{\varepsilon_{\mathrm{p}}(\mathbf{r}) + p^2/(2m_0)}{kT}\right] d\tau\, d\Omega$$

(5.6)

The constant factor C_N is

$$C_N = n(\mathbf{r}_1) \exp\left[\frac{\varepsilon_{\mathrm{p}}(\mathbf{r}_1)}{kT}\right] \frac{1}{(2\pi m_0 kT)^{3/2}}$$

To calculate it, we must know the concentration of the molecules for at least one point of space. There is another way of determining this quantity, which is often more convenient.

If we know the total number of particles N in the system being considered, then, since the integral of the distribution function over all the values of the momentum and the coordinates must equal the total number of particles, we obtain an equation determining C_N:

$$N = C_N \int \exp\left[-\frac{\varepsilon_{\mathrm{p}}(\mathbf{r}) + p^2/(2m_0)}{kT}\right] d\tau\, d\Omega$$

(5.7)

It is customarily called the **normalization condition**.

Hence, *when external force fields are present, the equilibrium distribution function has the form of* (5.6), *where the*

constant is determined by the condition (5.7). This distribution function combines the Maxwell distribution law in momentum space and the Boltzmann distribution law in conventional space and is therefore known as the **Maxwell-Boltzmann distribution function.**

5.2. Gibbs Distribution as a Generalization of the Maxwell-Boltzmann Distribution

In the following, we shall have to speak more and more often about particles whose coordinates are confined within the interval $d\tau$, and whose momentum components are confined within the interval $d\Omega$. To diminish formulations and in the long run to provide greater clarity, it will be good to introduce the notion of what is called the **phase space** of a particle or the **mu-space.**

The mu-space is defined to be a six-dimensional space in which the coordinates of a particle are laid off along three axes, and the components of its momentum along the other three. The position of a point in six-dimensional space is determined by six coordinates. Consequently, if a molecule is said to be at a point of phase space, this signifies that the space coordinates of the molecule are set, and also the components of its momentum. A volume element in mu-space, designated in the following by $d\gamma$, is set by the product of the differentials of all six of its coordinates, i.e.

$$d\gamma = dx\ dy\ dz\ dp_x\ dp_y\ dp_z = d\tau\ d\Omega. \qquad (5.8)$$

It can be seen from the above that when a particle is in the region $d\tau$ of conventional space, and its momentum is in the region $d\Omega$ of momentum space, this can be expressed briefly by saying that it is in the $d\gamma$ region of mu-space.

The Maxwell-Boltzmann distribution obtained in Sec. 5.1 from the viewpoint of the concept we have just introduced gives the mean number of molecules in the element $d\gamma$ of phase space, and formulas (5.6) and (5.7) can be rewritten in the form

$$dN = C_N \exp\left[-\frac{\varepsilon_p(\mathbf{r}) + p^2/(2m_0)}{kT} \right] d\gamma$$

$$N = C_N \int \exp\left[-\frac{\varepsilon_p(\mathbf{r}) + p^2/(2m_0)}{kT} \right] d\gamma \qquad (5.9)$$

Instead of exhibiting interest in the mean number of particles in $d\gamma$, we are sometimes interested in knowing the probability of one of them being within this volume. The relevant probability dW is

$$dW = \frac{dN}{N} = \frac{f\, d\gamma}{N}$$

The above expression shows that this probability is proportional to the phase space volume element $d\gamma$, i.e. the quantity $w = f/N$ has the meaning of the probability density. If we use the value of the Maxwell-Boltzmann distribution function and introduce the symbol $C_w = C_N/N$, we have

$$dW = w\,(\mathbf{r},\ \mathbf{p})\,d\gamma = \frac{f}{N}\,d\gamma = C_w \exp\left[-\frac{\varepsilon_p\,(\mathbf{r}) + p^2/\,(2m_0)}{kT} \right] d\gamma$$

or, taking into account that $\varepsilon = \varepsilon_p\,(\mathbf{r}) + p^2/(2m_0)$ is the total energy of a molecule, we obtain

$$dW = w\,(\mathbf{r},\ \mathbf{p})\,d\gamma = C_w \exp\left(-\frac{\varepsilon}{kT} \right) d\gamma \qquad (5.10)$$

The constant factor C_w is determined by the normalization condition for the probability density

$$\int dW = C_w \int \exp\left(-\frac{\varepsilon}{kT} \right) d\gamma = 1 \qquad (5.11)$$

Hence, *the Maxwell-Boltzmann probability density is given by relation* (5.10), *where the constant* C_w *is found from the normalization condition* (5.11).

Let us now consider the probability $dW\,(\mathbf{r}_1,\ \mathbf{p}_1;\ \mathbf{r}_2,\ \mathbf{p}_2)$ of the molecule *1* getting into the phase space volume element $d\gamma_1$, and the molecule *2* into the element $d\gamma_2$. If the interaction between them is negligibly small, the events are independent, and we have

$$dW\,(\mathbf{r}_1,\ \mathbf{p}_1;\ \mathbf{r}_2,\ \mathbf{p}_2) = dW\,(\mathbf{r}_1,\ \mathbf{p}_1)\,dW\,(\mathbf{r}_2,\ \mathbf{p}_2)$$

$$= C_w \exp\left(-\frac{\varepsilon_1}{kT} \right) d\gamma_1 \cdot C_w \exp\left(-\frac{\varepsilon_2}{kT} \right) d\gamma_2$$

$$= C_w^2 \exp\left(-\frac{\varepsilon_1 + \varepsilon_2}{kT} \right) d\gamma_1\, d\gamma_2$$

We can go further and determine the probability for all N molecules composing a gas. Indeed, assume that at a certain instant a gas is in a state such that the first molecule is

in the phase space volume element $d\gamma_1$, the second is in the element $d\gamma_2$, the third is in the element $d\gamma_3$ and so on up to the last molecule N in the element $d\gamma_N$. What is the probability of such a state of an ideal gas?

Considering as previously that all the molecules in an ideal gas move independently of one another (a sufficiently rarefied gas), it is not difficult to see that the total probability is

$$dW \left(\mathbf{r}_1, \ \mathbf{p}_1; \ \mathbf{r}_2, \ \mathbf{p}_2; \ \ldots; \mathbf{r}_N, \ \mathbf{p}_N\right)$$
$$= C_w^N \exp \left(-\frac{\varepsilon_1 + \varepsilon_2 + \ldots + \varepsilon_N}{kT} \right) d\gamma_1 \, d\gamma_2 \, \ldots \, d\gamma_N$$

The sum of the energies of all the molecules is the total energy of the gas, i.e.

$$\varepsilon_1 + \varepsilon_2 + \ldots + \varepsilon_N = \mathscr{E} \left(\mathbf{r}_1, \ \mathbf{p}_1; \ \mathbf{r}_2, \ \mathbf{p}_2; \ \ldots; \ \mathbf{r}_N, \ \mathbf{p}_N\right)$$

In the following, we shall write simply $\mathscr{E}$ without writing out all the arguments of this function, but always having in view that the total energy is a function of the positions and momenta of all N molecules in the system being considered.

It is also convenient to generalize the concept of phase space and consider not the mu-space, but the **total phase space** of the entire system—(the **gamma** or Γ-**space**). *The total phase space of a system consisting of N particles is defined to be a $6N$-dimensional space along whose axes $3N$ coordinates and $3N$ projections of the momenta of all the particles forming the system are laid off. A point in the total phase space determines the coordinates and momenta of all the particles and therefore completely determines the state of the system.* A volume element of the total phase space of a system, designated by $d\Gamma$, is

$$d\Gamma = dx_1 \, dy_1 \, dz_1 \, dp_{x1} \, dp_{y1} \, dp_{z1} \, \ldots$$
$$\ldots \, dx_N \, dy_N \, dz_N \, dp_{xN} \, dp_{yN} \, dp_{zN}$$
$$= d\tau_1 \, d\Omega_1 \, d\tau_2 \, d\Omega_2 \, \ldots \, d\tau_N \, d\Omega_N = d\gamma_1 \, d\gamma_2 \, \ldots \, d\gamma_N$$

Let us introduce still another symbol for the constant factor, i.e. C_w^N:

$$C_w^N = \exp \left(\frac{F}{kT} \right)$$

In other words, we determine the quantity F by the relation

$$F = kT \ln \left(C_w^N \right)$$

Now the total probability can be written in the following form known as the **Gibbs distribution:**

$$dW(\mathbf{r_1},\ \mathbf{p_1},;\ \ldots;\mathbf{r}_N,\ \mathbf{p}_N) = \exp\left(\frac{F-\varepsilon}{kT}\right)d\Gamma \quad (5.12)$$

It must be stressed that unlike the Maxwell-Boltzmann distribution that indicates the probability of a given state for one molecule of an ideal gas, the Gibbs distribution determines the probability of a state of a gas as a whole, i.e. of all its N molecules.

Formula (5.12), which is quite simple in appearance, conceals such a rich and profound content that it by right can be called the central relation of the entire statistical physics of equilibrium states. The matter is that although we have obtained this formula for an ideal gas, it actually, as shown by J. Gibbs, holds for any system.

In constructing the theory of each branch of physics, it is usually convenient to choose a few fundamental propositions as the basis that makes it possible to explain all the phenomena relating to this branch. The correctness of the fundamental propositions is established either by direct experimental verification, or indirectly by verifying whether or not all the conclusions reached on their basis correspond to experimental data. For example in mechanics, the role of the main propositions is played by Newton's laws. In electrodynamics, a group of equations known as Maxwell's equations are taken as the basic ones. Similarly, in the statistical physics of equilibrium states, the Gibbs distribution can be taken as a fundamental proposition, and, consequently, all the properties of systems that are in equilibrium are obtained because of the correctness of this distribution.

The Gibbs distribution determining the probability of an equilibrium system being in one of the states belonging to a volume element $d\Gamma$ *of the phase space of the system is given by formula* (5.12), *where $\mathscr{E}$ is the energy of the system in a state from* $d\Gamma$ *represented as a function of the position and momenta of all the particles forming the system, T is the temperature, and F is a quantity known as the free energy and determined by the normalization condition* (5.13):

$$\int dW = \int \exp\left(\frac{F-\mathscr{E}}{kT}\right)d\Gamma = \exp\left(\frac{F}{kT}\right)$$
$$\times \int \exp\left(-\frac{\mathscr{E}}{kT}\right)d\Gamma = 1 \quad (5.13)$$

or

$$F = -kT \ln Z \qquad (5.14)$$

where

$$Z = \int \exp\left(-\frac{\mathscr{E}}{kT}\right) d\Gamma \qquad (5.15)$$

is a quantity called the **state integral.**

5.3. Example of a Monatomic Ideal Gas

Let us again consider a monatomic ideal gas as the first example of application of the Gibbs distribution. Although we already know the result in this case, our aim is to show how the Gibbs distribution is applied to a specific problem. For this reason, we shall not take into account all the previously obtained results, but shall use only the Gibbs distribution and information on the system being considered.

If a total of N molecules of an ideal gas are in a vessel which they cannot emerge from, we may consider them to be in the field of external forces whose potential energy forms a well of infinite depth. Indeed, the potential energy of a molecule in a vessel is constant, and it may be considered to equal zero. In addition, to extract a molecule, we must spend an infinitely great amount of work so that the potential energy outside the vessel is virtually infinite.

At a given temperature T, the probability of a state of a gas from among the number of states described by points of the phase space volume element $d\Gamma$ is determined by the Gibbs distribution (5.12). To apply this formula to an ideal gas means to indicate the value of the quantities $\mathscr{E}$ and F for this specific case.

In an ideal gas, the molecules do not interact with one another, therefore the total energy $\mathscr{E}$ equals the sum of the energies of the individual molecules:

$$\mathscr{E} = \sum_{i=1}^{N} \varepsilon_i \qquad (5.16)$$

The energy of a molecule equals the sum of its kinetic and potential energies, i.e.

$$\varepsilon_i = \frac{p_i^2}{2m_0} + \varepsilon_{\mathbf{p}, i} \qquad (5.17)$$

where the potential energy $\varepsilon_{p,\,i}$ is a position function of the i-th molecule that equals zero inside the vessel (well) and infinity outside it. Hence,

$$\mathscr{E} = \sum_{i=1}^{N} \left[\frac{p_i^2}{2m_0} + \varepsilon_{p,\,i}\,(\mathbf{r}) \right] \tag{5.18}$$

It remains to find the value of the free energy F, and then all the quantities determining the Gibbs distribution for a given specific problem will be known. Since the free energy is expressed quite simply in terms of the state integral Z, everything reduces to calculating the latter. Both in this and in all other problems of statistical physics, it is exactly here that the main difficulties are concentrated.

According to the definition of the state integral (5.15), using the property of an ideal gas expressed by formula (5.16), we can write

$$Z = \int \exp\left(-\frac{\mathscr{E}}{kT} \right) d\Gamma = \underbrace{\int \ldots \int}_{N} \exp\left(-\frac{\sum\limits_{i=1}^{N} \varepsilon_i}{kT} \right) d\gamma_1 \ldots d\gamma_N \tag{5.19}$$

The $6N$-dimensional integral in (5.19) is written as the product of N six-dimensional integrals:

$$Z = \int \exp\left(-\frac{\varepsilon_1}{kT} \right) d\gamma_1 \int \exp\left(-\frac{\varepsilon_2}{kT} \right) d\gamma_2$$
$$\ldots \int \exp\left(-\frac{\varepsilon_N}{kT} \right) d\gamma_N \tag{5.20}$$

and this allows us to complete the calculations. Indeed, all the integrals in (5.20) are the same and differ only in the designation of the integration variables, which naturally does not affect their value. Hence,

$$Z = \left[\int \exp\left(-\frac{\varepsilon_1}{kT} \right) d\gamma_1 \right]^N \tag{5.21}$$

Let us designate the integral in brackets in (5.21) by z and evaluate it:

$$z = \int \exp\left(-\frac{\varepsilon_1}{kT} \right) d\gamma_1$$
$$= \int \exp\left[-\frac{p_1^2/\,(2m_0)+\varepsilon_{p1}}{kT} \right] d\tau_1\, d\Omega_1$$

Writing the integral in the form

$$z = \int \exp\left(-\frac{p_1^2}{2m_0\,kT}\right) d\Omega_1 \int \exp\left(-\frac{\varepsilon_{p1}}{kT}\right) d\tau_1 \quad (5.22)$$

we reduce the problem to the evaluation of two three-dimensional integrals. The first was encountered in studying the Maxwell distribution and was evaluated, it equals $(2\pi m_0 kT)^{3/2}$. This expression follows from the normalization condition for the Maxwell distribution taken in the form of the last of Eqs. (3.21).

The value of the second integral is found even more simply. Since outside the vessel $\varepsilon_{p1} = \infty$, the relevant integrand is zero. Inside the vessel, $\varepsilon_{p1} = 0$, so that the integrand equals unity. Hence, what remains is the integral with respect to $d\tau_1$ taken over the volume of the vessel, i.e.

$$\int d\tau_1 = V$$

where V is the volume of the vessel containing the gas.

We thus obtain

$$Z = z^N = V^N \, (2\pi m_0 kT)^{(3/2)\,N} \quad (5.23)$$

and, therefore,

$$F = -kT \ln Z = -kT\,N$$
$$\times \left[\ln V + \frac{3}{2}\ln T + \frac{3}{2}\ln(2\pi m_0 k)\right] \quad (5.24)$$

Attention is drawn to the fact that, as can well be seen from formula (5.24), the free energy F is a function of variables such as the volume occupied by a system and its temperature, but at the same time it must be treated as a constant quantity if we have in view the dependence on the coordinates and momenta of individual molecules.

Hence, *in the Gibbs distribution for a monatomic ideal gas, the energy is determined by formula* (5.18), *and the free energy, by formula* (5.24). Knowing the Gibbs distribution, i.e. the probability of different states of a system, we can calculate the mean value of any physical quantities. It will be shown in the following chapter that most of them are found quite simply directly from the free energy F of the system.

For better mastering of the meaning of the Gibbs distribution, let us consider the following numerical example. Assume that we have a monatomic gas, for example, helium,

with 10^{20} molecules occupying a volume V equal to one litre at 27 °C. In these conditions, the gas may be considered ideal. What is the probability of a state in which all N molecules will be concentrated in a region of the vessel forming 0.1 of the entire volume, with their velocities having a virtually identical value, namely, ranging from 300 to 301 m/s? The answer is given by formula (5.12). In it

$$d\Gamma = d\tau_1 \, d\Omega_1 \, d\tau_2 \, d\Omega_2 \, \ldots \, d\tau_N \, d\Omega_N$$

here

$$d\tau_1 = d\tau_2 = \ldots = d\tau_N = 0.1 V_1$$

and

$$d\Omega_1 = d\Omega_2 = \ldots = d\Omega_N = 4\pi p^2 \, dp = 4\pi v^2 \, dv m_0^3$$

where $v = 300$ m/s (or 301 m/s), $dv = 1$ m/s, $m_0 = 4.68 \times 10^{-27}$ kg, so that $d\Omega = 1.17 \times 10^{-73}$ kg³m³s⁻³.

The energy of the given state is

$$\mathscr{E} = \sum_{i=1}^{N} p_i^2 \, (2m_0) = \frac{Np^2}{2m_0} = 2.1 \times 10^{-2} \text{ J}$$

The free energy is calculated by formula (5.24). In the present case, it is convenient to write it in the form

$$F = \ln \left[\frac{1}{V} \, \frac{1}{(2\pi m_0 \, kT)^{3/2}} \right]^{NkT}$$

then the exponential factor in the Gibbs formula yields

$$\exp \left(\frac{F - \mathscr{E}}{kT} \right) = \frac{1}{V^N} \, \frac{1}{(2\pi m_0 \, kT)^{(3/2)N}} \exp \left(-\frac{\mathscr{E}}{kT} \right)$$

The factor

$$(2\pi m_0 kT)^{3/2}$$

by analogy with the factor V can be considered as the effective volume in the momentum space available for the molecules at the temperature T. Its numerical value in the given example is 4.27×10^{-32} kg³m³s⁻³.

We finally obtain

$$dW = \exp \left(\frac{F - \mathscr{E}}{kT} \right) d\Gamma = \left(\frac{0.1V}{V} \right)^N$$

$$\times \left[\frac{4\pi v^2 \, d \, vm_0^3}{(2\pi m_0 \, kT)^{3/2}} \right]^N \exp \left(-\frac{\mathscr{E}}{kT} \right)$$

The factor $(0.1V/V)^N = 10^{-N}$ corresponds to the probability of all the molecules being concentrated in the volume

0.1V. This probability is exceedingly low, as was already shown in Sec. 3.1. The second factor

$$\left[\frac{4\pi v^2 \ d \ v m_0^3}{(2\pi m_0 \ kT)^{3/2}} \right]^N \exp \left(- \frac{\mathscr{E}}{kT} \right)$$

determines the probability of the velocities of all the molecules being within the interval considered. It is also very low. Inspection of the results obtained shows that the probability of the chosen state is extremely small. The explanation is that the total number of states of the system including 10^{20} particles is extraordinarily large (the phase volume per particle is assumed to be the same for all states).

5.4. Maxwell-Boltzmann Distribution

If we adopt the Gibbs distribution as the fundamental postulate of the statistical physics of equilibrium states, it is quite simple to obtain the Maxwell momentum distribution and the Boltzmann coordinate distribution with its aid. Here there is no need in the rather long and not completely substantiated reasoning that led us to the Maxwell-Boltzmann distribution in Chaps. 3 and 4.

Let us take a single molecule of an ideal gas as our system. The phase space of the "system" coincides here with that of one particle, so that $d\Gamma = d\gamma$. For the probability of a given state of the system consisting of one molecule, the Gibbs formula yields

$$dW = \exp \left(\frac{F - \mathscr{E}}{kT} \right) d\gamma \tag{5.25}$$

where $\mathscr{E} = p^2/(2m_0) + \varepsilon_p (\mathbf{r})$ is the energy of the molecule.

Expression (5.25) can be written in a form in which it is clearly shown that it coincides with the Maxwell-Boltzmann distribution:

$$dW = C_w \exp \left(- \frac{p^2}{2m_0 \ kT} \right) \exp \left(- \frac{\varepsilon_p (\mathbf{r})}{kT} \right) d\tau \ d\Omega$$

where the normalization constant $C_w = \exp [F/(kT)]$ is determined by the equation

$$C_w = \left[\int \exp \left(- \frac{p^2}{2m_0 \ kT} \right) d\Omega \cdot \int \exp \left(- \frac{\varepsilon_p (\mathbf{r})}{kT} \right) d\tau \right]^{-1}$$

$$= (2\pi m_0 \ kT)^{3/2} \left[\int \exp \left(- \frac{\varepsilon_p}{kT} \right) d\tau \right]^{-1}$$

Final calculation of C_w is possible if the potential energy of the molecule is given. For example, if the molecule is in a container and there are no other external forces except those acting from the side of the walls, we have

$$\int \exp\left(-\frac{\varepsilon_p}{kT}\right) d\tau = V$$

where V is the volume of the container, and

$$C_w = \frac{1}{(2\pi m_0 kT)^{3/2}} \frac{1}{V}$$

When we consider a gas column with a base area of S in the Earth's gravitational field ($\varepsilon_p = m_0 gz$), we have

$$\int \exp\left(-\frac{\varepsilon_p}{kT}\right) d\tau = \int dx \int dy \int dz \exp\left(-\frac{mgz}{kT}\right)$$

$$= S\frac{kT}{m_0 g} = SH_{\text{eff}}$$

and

$$C_w = \frac{1}{(2\pi m_0 kT)^{3/2}} \frac{1}{SH_{\text{eff}}}$$

The above example may be insufficient to convince one of the expediency of choosing the Gibbs distribution as the foundation for constructing the statistical physics of equilibrium states because here we simply repeated all our previous calculations used to substantiate it. On a later page, however, in particular in quantum statistics, one of the forms of the Gibbs distribution will be used to obtain new results.

Assume that we are interested in particles of so high energies that their velocity is close to the speed of light c. It is natural that to determine the statistical characteristics of such particles, the Maxwell distribution, which takes no account of the effects of the theory of relativity, cannot be applied. What is the momentum distribution of particles when relativistic effects are taken into account? The answer is obtained quite easily with the aid of the Gibbs distribution.

Again choosing a single particle as a system, we find

$$dw = C_w \exp\left(-\frac{\varepsilon}{kT}\right) d\Omega \, d\tau$$

If the particle is in a potential well, outside the latter its energy is infinite, while inside the well it is determined by the well known Einstein formula $\varepsilon = mc^2$, where $m = = m_0/\sqrt{1 - v^2/c^2}$ is the mass of the particle depending on the velocity, and m_0 is its rest mass.

In the theory of relativity, the momentum is

$$\mathbf{p} = m\mathbf{v} = \frac{m_0\mathbf{v}}{\sqrt{1 - v^2/c^2}} \qquad (5.26)$$

Using Eq. (5.26) to express the velocity in terms of the momentum, we find

$$v^2 = \frac{p}{m_0^2 + p^2/c^2}$$

If we now introduce this expression into the one for the energy, we obtain the latter as a function of the momentum:

$$\varepsilon = \frac{m_0 c^2}{\sqrt{1 - v^2/c^2}} = \frac{m_0 c^2}{\sqrt{1 - p^2/[c^2(m_0^2 + p^2/c^2)]}}$$

$$= m_0 c^2 \sqrt{1 + \frac{p^2}{m_0^2 c^2}}$$

Hence,

$$\mathrm{d}w = C_w \exp\left[-\frac{m_0 c^2 \sqrt{1 + p^2/(m_0^2 c^2)}}{kT}\right] \mathrm{d}\Omega \, \mathrm{d}\tau \qquad (5.27)$$

inside the well and is zero outside it. The constant C_w is determined by the expression

$$C_w = \frac{1}{V}\left\{\int_0^\infty \exp\left[-\frac{m_0 c^2 \sqrt{1 + p^2/(m_0^2 c^2)}}{kT}\right] 4\pi p^2 \, \mathrm{d}p\right\}^{-1}$$

or

$$C_w = \frac{1}{V} \frac{1}{4\pi m_0^3 c^3}\left\{\int_0^\infty \exp\left[-\frac{m_0 c^2}{kT}\sqrt{1 + y^2}\right] y^2 \, \mathrm{d}y\right\}^{-1} \qquad (5.28)$$

where $y = p^2/(m_0^2 c^2)$. The integral

$$f = \int_0^\infty \exp\left(-\frac{m_0 c^2}{kT}\sqrt{1 + y^2}\right) y^2 \, \mathrm{d}y$$

cannot be evaluated in elementary functions, but it depends on the single parameter $\zeta = kT/(m_0 c^2)$, and the graph in Fig. 5.1 shows such a relation obtained by numerical integration.
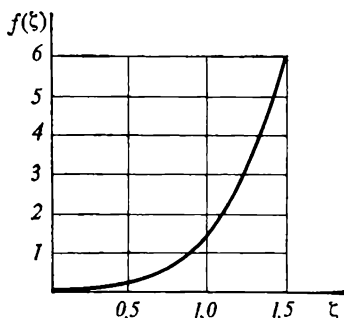
Fig. 5.1

In the cases usually encountered, the value of the parameter is low ($\zeta \ll 1$), the exponential rapidly falls off even at low values of y, and, therefore, assuming in the exponent that

$$\sqrt{1+y^2} \approx 1 + \frac{y^2}{2}$$

we find

$$f \approx \exp\left(-\frac{m_0 c^2}{kT}\right) \int\limits_0^\infty \exp\left(-\frac{m_0 c^2}{2kT} y^2\right) y^2 \, dy$$

$$= \sqrt{2\pi} \exp\left(-\frac{m_0 c^2}{kT}\right) \left(\frac{kT}{m_0 c^2}\right)^{3/2} = \sqrt{2\pi} \exp\left(-\frac{1}{\zeta}\right) \zeta^{3/2}$$

At large values of the parameter ($\zeta \gg 1$), the exponential appreciably diminishes only at values of $y \gg 1$, and, therefore,

$$f \approx \int\limits_0^\infty \exp\left(-\frac{m_0 c^2}{kT} y\right) y^2 \, dy = 2\left(\frac{kT}{m_0 c^2}\right)^3 = 2\zeta^3$$

It thus follows from what has been said in the present section that *the Gibbs distribution directly leads to the Maxwell-Boltzmann distribution, and other distributions can be obtained quite simply with its aid.* Examples are distributions taking effects of the theory of relativity into account.

5.5. Uniform Distribution of Energy among Degrees of Freedom

In applications, it is often important to know the mean value of the energy of a system or of the individual molecules forming the system. It was found that there is a very simple and convenient expression for the mean value of the kinetic energy, and we shall now treat it.

Up to now, we considered the molecules to be point particles for which the kinetic energy is

$$\varepsilon_k = \frac{p^2}{2m_0} = \frac{p_x^2 + p_y^2 + p_z^2}{2m_0}$$

In Chap. 3, we found with the aid of the Maxwell distribution [see (3.22)] that $\langle p_x^2 \rangle = m_0 kT$, so that we obtain the following expression for the mean value of the kinetic energy corresponding to motion along the x-axis:

$$\langle \varepsilon_{kx} \rangle = \frac{\langle p_x^2 \rangle}{2m_0} = \frac{kT}{2} \tag{5.29}$$

Exactly similar equations are also obtained for the kinetic energy of motion along the y- and z-axes:

$$\langle \varepsilon_{ky} \rangle = \langle \varepsilon_{kz} \rangle = \frac{kT}{2} \tag{5.30}$$

The mean value of the total kinetic energy is

$$\langle \varepsilon_k \rangle = \langle \varepsilon_{kx} \rangle + \langle \varepsilon_{ky} \rangle + \langle \varepsilon_{kz} \rangle = \frac{3}{2} kT \tag{5.31}$$

Formulas (5.29) and (5.30) can be interpreted to mean that the same mean kinetic energy equal to $kT/2$ falls to each degree of freedom of a particle. For a point particle having three degrees of freedom, the mean value of the kinetic energy is $\frac{3}{2} kT$. This result is a particular case of a very general rule according to which *a mean kinetic energy equal to $kT/2$ falls to each degree of freedom of any classical system in equilibrium.*

For example, if we consider a gas consisting of polyatomic molecules, the latter must be treated not as point particles, but rather as rigid bodies having finite, though small, dimensions. A rigid body has a total of six degrees of freedom. Indeed, the position of the centre of mass of a rigid body is set by three coordinates, which corresponds to three degrees

of freedom of translational motion, while its position in rotation about the centre of mass is determined by three other coordinates, usually by the Euler angles. The angular coordinates characterize three additional rotational degrees of freedom. Hence, the mean kinetic energy of translational motion of the molecules in a gas equals $N \cdot \frac{3}{2} kT$, and the same energy corresponds to their rotation, so that the total mean kinetic energy is

$$\langle \varepsilon_k \rangle = 6N \, \frac{kT}{2} = 3NkT$$

The complete proof of the theorem of equipartition of the kinetic energy among the degrees of freedom is quite cumbersome, and it is therefore given in Appendix 3 instead of in the text.

In the general case, the result obtained for the kinetic energy does not hold for the potential energy. For the elastic potential energy that is a quadratic position function, however, the mean value is also $kT/2$ for each degree of freedom corresponding to a definite coordinate. For instance, for one-dimensional motion along the x-axis, the elastic potential energy is

$$\varepsilon_p = \frac{\varkappa x^2}{2}$$

where $\varkappa$ is the **rigidity**, and the mean value of the potential energy is

$$\langle \varepsilon_p \rangle = \frac{\varkappa \langle x^2 \rangle}{2} = \frac{kT}{2} \tag{5.32}$$

For the three-dimensional case, we have

$$U = \frac{\varkappa_1 x^2}{2} + \frac{\varkappa_2 y^2}{2} + \frac{\varkappa_3 z^2}{2}$$

$$\langle U \rangle = \frac{3 \, kT}{2}$$

The theorem of equipartition of energy was a major achievement of classical statistical physics, but by a comparison with experimental data it also showed that classical statistics has a limited application. Indeed, its application made it possible to explain quite simply the difference in the heat capacities of monatomic, diatomic, and polyatomic ideal gases. Since the internal energy of an ideal gas is the

mean value of the kinetic energy of its molecules, according to the equipartition theorem we have

$$U = N \frac{i}{2} kT \qquad (5.33)$$

where i is the number of degrees of freedom of a molecule. Three degrees of freedom per atom should be ascribed to a monatomic gas because the position of an atom is determined by three coordinates. The position of a diatomic molecule in space can be indicated by setting the position of its centre of mass (three degrees of freedom) and two angles determining the direction of its axis in space (two more degrees of freedom). Hence, for a diatomic molecule, i equals five. Finally, a polyatomic molecule, if treated as a small rigid body, has six degrees of freedom of which three correspond to translational motion and three to rotation. The additional degree of freedom in comparison with a diatomic molecule can be considered as corresponding to the angle of rotation about the axis whose direction is set by two other coordinates.

Relation (5.33) in a number of cases agrees quite well with experimental results. This seems to confirm the correctness of theory. A more attentive consideration of this matter, however, shows that if the theorem of equipartition of energy were unconditionally correct, there would be no coincidence with experimental data. To convince oneself that this is true, it is sufficient, for example, to take into account that atoms consist of nuclei and electrons orbiting around them. If we take into account the degrees of freedom relating to the individual electrons, the mean kinetic energy of an atom would have to be considerably greater.

5.6. Fluctuations in Measuring Instruments

To illustrate the general nature of the Gibbs distribution, we shall show how it allows us to solve quite simply the problem of the fluctuations of instrument readings, which is very important in practice. We shall begin our discussion with the very simple mechanical system shown in Fig. 5.2. The system consists of the mass m fastened to a spring whose rigidity (spring constant) is $\varkappa$ and is a model followed by many instruments. For example, a galvanometer consists of

a pointer (mass) and a helical spring that returns the pointer to its equilibrium position. In an analytical balance, the mass of the movable system is returned to its equilibrium position by the force of gravity whose moment is proportional to the angle characterizing the deviation from the
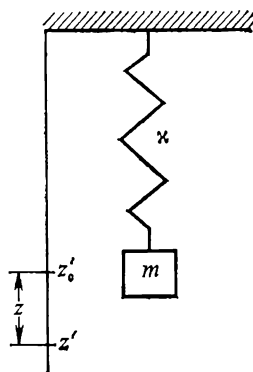
Fig. 5.2

equilibrium position, i.e. in this meaning the moment of the force of gravity is similar to the elastic force of a spring. Other examples could also be given.

The equation of motion of the spring balance shown in Fig. 5.2 has the form

$$m\ddot{z}' = -\varkappa z' - \eta \dot{z}' + F + mg \qquad (5.34)$$

(here z' is the coordinate of the mass m, $-\varkappa z'$ is the elastic force of the spring, $-\eta \dot{z}'$ is the force of friction appearing when the mass moves in the medium surrounding it, F is the external force being measured, and mg is the force of gravity acting on the mass). When the system is at rest, we have $\dot{z}' = \ddot{z}' = 0$, and it follows from Eq. (5.34) that

$$z_0' = \frac{mg + F}{\varkappa}$$

The coordinate z_0' corresponds to equilibrium of the mass under the action of the forces applied to it.

It is convenient for our further treatment to introduce the coordinate $z = z' - z_0'$ characterizing the deviation

from the equilibrium position. Now the equation of motion
becomes

$$m\ddot{z} + \eta\dot{z} + \varkappa z = 0 \qquad (5.35)$$

The term $\eta\dot{z}$ in Eq. (5.35) is of paramount importance for
the fluctuations being considered here, i.e. for the chaotic
thermal fluctuations of the spring balance pointer m. This
term describes the interaction of the pointer with the sur-
rounding medium. The interaction roughly consists in bom-
bardment of the pointer by the molecules of the medium,
which are in thermal equilibrium at the temperature T.
On an average, all the directions of the impacts are equally
probable, therefore the mean reading of the scale is zero:
$\langle z \rangle = 0$. If the pointer is brought into motion, the oncom-
ing impacts begin to prevail, and the mass experiences
counteraction to its motion described by the term with the
force of friction $\eta\dot{z}$. When the balance is in equilibrium, the
impacts are compensated by one another only on an average.
Since at a certain instant the result of bombarding the bal-
ance by the molecules of the medium from one side may be
greater than from the other one, and at the next instant
the reverse may occur, attentive observation should reveal
the continuous chaotic motion of the pointer so that its
coordinate z equals zero only on an average. The magnitude
of the deviations, i.e. the magnitude of the fluctuations, is
customarily characterized by the **mean square deviation**
$\langle z^2 \rangle$ from the position of equilibrium (**the mean square
fluctuation**).

From the viewpoint of statistics, the problem of the spring
balance is similar to the problem of a large molecule of
mass m in the field of an elastic force with the potential ener-
gy $\varkappa z^2/2$ equal to that of a compressed spring. Because of
contact with the medium, the balance is in thermal equilib-
rium at the temperature T. Its state can be characterized
by the position of the pointer (the coordinate z) and its
momentum $(m\dot{z})$. According to Gibbs, the probability of
the pointer being in the interval dz and having a momentum
within the interval d $(m\dot{z})$ is given by the expression

$$dW = \exp\left(\frac{F - \mathscr{E}}{kT}\right) d\Gamma = \exp\left(\frac{F - \mathscr{E}}{kT}\right) dz \, d\,(m\dot{z})$$

where $\mathscr{E} = m\dot{z}^2/2 + \varkappa z^2/2$ is the energy of the pointer equal to the sum of the kinetic and potential energies.

The magnitude of the fluctuations is determined by the general expression

$$\langle z^2 \rangle = \int z^2 \exp\left(\frac{F-\mathscr{E}}{kT}\right) d\Gamma$$

but in the given case it can be evaluated more easily by taking advantage of the energy equipartition theorem. Indeed, the conditions stipulated in Sec. 5.5 are observed for the potential energy, and therefore

$$\frac{\langle \varkappa z^2 \rangle}{2} = \frac{\varkappa}{2}\langle z^2 \rangle = \frac{kT}{2}, \quad \text{i.e.} \quad \langle z^2 \rangle = \frac{kT}{\varkappa} \qquad (5.36)$$

Numerical assessments show (see Example 1 to the present chapter) that in actually realized mechanical systems the
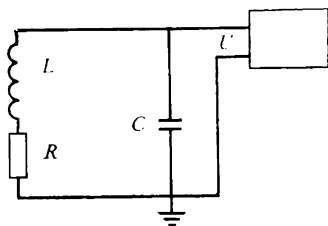
Fig. 5.3

magnitude of the fluctuations is very small so that they may affect the accuracy of measurement only in exclusive cases.

Matters are absolutely different in electrical measuring circuits where the sensitivity of the receiving and amplifying equipment is quite often limited by thermal fluctuations. Assume that at the input of an amplifier with a large amplification factor an oscillatory circuit is arranged as shown in Fig. 5.3. The voltage U, related to the charge Q by the expression

$$Q = CU \qquad (5.37)$$

where C is the capacitance of the capacitor, is fed from the plates of the latter to the first stage of the amplifier. If the amplification factor is made sufficiently large and the output voltage is fed to an oscillograph, chaotic oscillations

that are the thermal fluctuations of the voltage across the capacitor will be observed on the screen.

The equation describing the behaviour of an oscillatory circuit has the form

$$IR + U = -L\frac{dI}{dt} \qquad (5.38)$$

and signifies that the sum of the voltage across the capacitor and the voltage drop across the resistor with the resistance R equals the e.m.f. of self-induction of the coil with the inductance L acting in the circuit. With a view to the current I in the circuit being related to the charge of the capacitor by the expression

$$\frac{dQ}{dt} = I \qquad (5.39)$$

we can rewrite Eq. (5.38) in the form

$$L\frac{d^2Q}{dt^2} + R\frac{dQ}{dt} + \frac{Q}{C} = 0 \qquad (5.40)$$

where Q/C has been substituted for U in accordance with (5.37).

The analogy of Eq. (5.40) to Eq. (5.35) is striking. This analogy has a deep meaning. The term containing the resistance R plays the same role as the relevant term containing the coefficient of friction η in (5.35), i.e. it is exactly this term that underlies the interaction of the electrical oscillations in the circuit with the thermal motion of the atoms of the crystal lattice in the material which the resistor is made from. The lattice atoms form a heat bath, and as a result of their collisions with electrons, the latter acquire a state of disordered chaotic motion. If a larger number of electrons begin to move in one direction, the capacitor is charged in accordance with this direction of the current. At the following instant, a larger number of electrons moves in the opposite direction, and the capacitor becomes recharged. Hence, the direct cause of electrical fluctuations appearing in the circuit are the random motions of the electrons in the resistor due to its interaction with the heat bath (crystal lattice).

The state of the electrical oscillations in the circuit is set if the values of the charge Q (coordinate) and the current I (velocity) are known. The total energy of a circuit in

a certain definite state equals the sum of the electrical and magnetic energies:

$$\mathscr{E} = \frac{Q^2}{2C} + \frac{LI^2}{2} \qquad (5.41)$$

where the electrical energy $Q^2/(2C)$ is similar to the potential energy $\varkappa z^2/2$, and the magnetic energy $LI^2/2$, to the kinetic energy $m\dot{z}^2/2$. According to the **Gibbs principle,** *the probability of the charge of a capacitor in a circuit having a value within the interval from Q to $Q + dQ$, and the current—a value within the interval from I to $I + dI$, is determined by the Gibbs distribution*

$$dW = \exp\left(\frac{F - \mathscr{E}}{kT}\right) d\Gamma \qquad (5.42)$$

where the right-hand side of (5.41) should be substituted for $\mathscr{E}$, and $d\Gamma = dQ\, dI$.

Now we are able to calculate the mean-square voltage across the capacitor:

$$\langle U^2 \rangle = \frac{\langle Q^2 \rangle}{C^2}$$

where the mean value $\langle Q^2 \rangle$ is determined with the aid of the Gibbs distribution (5.42) or even more simply with the aid of the theorem of equipartition of energy:

$$\frac{\langle Q^2 \rangle}{2C} = \frac{kT}{2}$$

A glance at the last two relations shows that

$$\langle U^2 \rangle = \frac{kT}{C} \qquad (5.43)$$

Formula (5.43) answers the question on the magnitude of the fluctuations, but it is convenient to transform it somewhat by expressing the capacitance in terms of the resistance and the transmission bandwidth of the circuit. Using methods of electrical engineering, we can show that

$$\frac{1}{C} = 4 z_R \, \Delta\nu$$

where $\Delta\nu$ is the bandwidth which the circuit is tuned to, and $z_R = L/(RC)$ is its (ohmic) resistance at the resonance frequency. Hence, the basic expression relating the mean

square of the voltage thermal fluctuations to the temperature and circuit parameters is

$$\langle U^2 \rangle = 4kTz_R \, \Delta v$$

For example, in a receiver with a bandwidth of $\Delta v = 10 \, \text{kHz}$ operating at a normal temperature of $T = 300 \, \text{K}$ and having an input resistance of $z_R = 10 \, \text{k}\Omega$, the root-mean-square value of the noise voltage is

$$\sqrt{\overline{\langle U^2 \rangle}} = \sqrt{\overline{4kTz_R \, \Delta v}} \approx 1.3 \mu \text{V}$$

If the input signal is lower than this value, it cannot be distinguished against the background of the chaotic thermal oscillations.

5.7. Real Gas

Let us consider as another example the application of the Gibbs distribution to a real gas, i.e. to a gas in which account is taken of the interaction between its constituent atoms or molecules. Although this problem cannot be solved exactly, even an approximate approach, however, makes it possible to obtain a number of interesting results, which will be shown on a later page (see Sec. 6.7).

The energy of a system of interacting atoms can be written as

$$\mathscr{E} = \sum_i \frac{p_i^2}{2m_0} + \frac{1}{2} \sum_{i \neq k} \varepsilon_{ik} + \sum_i \varepsilon_i \qquad (5.44)$$

where ε_i is the potential energy of the i-th atom in the field of the external forces, and ε_{ik} is the potential energy of interaction of the i-th and k-th atoms. The sum is evaluated over all the values of i and k that do not equal each other. The factor $1/2$ takes into account that in the sum over i and k, the energy of interaction between each pair of atoms is written twice. For instance, the energy of interaction of the third and fifth atoms is included once as the term ε_{35}, and a second time as ε_{53}.

The properties of a real system depend on the interaction energy ε_{ik}. The latter, in turn, is a sufficiently complicated function of the interatomic distance r_{ik}. This functional relation is illustrated from a qualitative viewpoint in

Fig. 5.4. The meaning of the graph can be explained as follows. At large interatomic distances, atoms do not virtually interact, and the energy ε_{ik} may be taken equal to zero. At smaller distances, forces of mutual attraction appear that tend to bring the atoms closer. Since these forces perform positive work, this signifies that the mutual potential energy of the atoms diminishes, i.e. becomes negative. At very small distances, when the electronic shells of the atoms begin to overlap appreciably, repulsion forces manifest themselves, and they increase very rapidly with diminishing r_{ik}. To
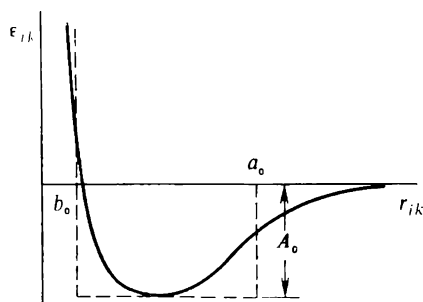
Fig. 5.4

bring the atoms closer, considerable external forces must now be applied to them that do positive work, i.e. increase the energy ε_{ik}. It is convenient to replace the real plot of ε_{ik} against r_{ik} with an approximate one shown by a dashed line in Fig. 5.4. The quantity b_0 corresponds to the minimum possible distance between atoms and, consequently, can be treated as the diameter of a "rigid" atom. The parameter A_0 has the meaning of the work needed to separate one atom from another, and the quantity a_0 can be interpreted as the "range of action" of the attraction forces. The choice of the parameters b_0, A_0, and a_0 is arbitrary to a certain extent and is limited only by the requirement that the real and approximating relations be as close to each other as possible.

For the Gibbs distribution to be considered as known, all we have to do is to compute the free energy F or, which in essence is equivalent to this, the state integral Z; the latter

with a view to (5.44) has the following form

$$Z = \int \exp\left(-\frac{\mathscr{E}}{kT}\right) d\Gamma$$

$$= \int \exp\left[-\frac{\sum\limits_{i} p_i^2/(2m_0) + \frac{1}{2}\sum\limits_{i \neq k} \varepsilon_{ik} + \sum\limits_{i} \varepsilon_i}{kT}\right] d\Gamma \quad (5.45)$$

The first sum in the exponent depends only on the momenta, while the second and third sums depend only on the coordinates. Hence, (5.45) is divided into two integrals—over the momenta and over the coordinates:

$$Z = \int \exp\left[-\frac{\sum\limits_{i} p_i^2/(2m_0)}{kT}\right] d\mathbf{p}_1 \ldots d\mathbf{p}_N$$

$$\times \int \exp\left[-\frac{\frac{1}{2}\sum\limits_{i \neq k} \varepsilon_{ik} + \sum\limits_{i} \varepsilon_i}{kT}\right] d\mathbf{r}_1 \ldots d\mathbf{r}_N$$

The integral over the momenta coincides with the one evaluated for an ideal gas (see Sec. 5.3). It equals

$$\int \exp\left[-\frac{\sum\limits_{i} p_i^2}{2m_0 kT}\right] d\mathbf{p}_1 \ldots d\mathbf{p}_N = (2\pi m_0 kT)^{3N/2}$$

Let us consider in greater detail the integral over the coordinates. If a gas is in a vessel whose volume is V, then the energies ε_i, as was done for an ideal gas, may be considered equal to zero inside the vessel and infinite outside it, so that for outside the vessel the exponential vanishes. Consequently, the integral is actually evaluated only over the volume of the vessel, and thus all the ε_i's should be considered to equal zero. The integral acquires the form

$$J_N = \int\limits_{V} \ldots \int\limits_{V} \exp\left(-\frac{\frac{1}{2}\sum\limits_{i \neq k} \varepsilon_{ik}}{kT}\right) d\mathbf{r}_1 \ldots d\mathbf{r}_N \quad (5.46)$$

Assume the volume V to be so large (the concentration is so low) that events consisting in the "sticking together" of three or more atoms are very rare. Now, the integral (5.46) can be evaluated approximately as follows. Let us fix the

coordinates of the $(N-1)$-atom and integrate over the coordinates of the last atom numbered N. When the atom N is at a distance from the other atoms that is larger than the range of action of the attraction forces, the potential energy is zero, so that the exponential equals unity, and integration yields the volume of the vessel less the volume of the spheres of attraction of all the other atoms. When the N-th atom is in the sphere of attraction, the exponential equals the constant quantity $\exp(A_0/kT)$, and integration gives the volume of all the regions where $\varepsilon_{ik} = -A_0$, multiplied by $\exp(A_0/kT)$. Hence, disregarding the intersection of the spheres of attraction, after integration over the coordinates of the N-th atom, we obtain

$$J_N = \Big[V - (N-1)\, \frac{4}{3}\, \pi a_0^3$$

$$+ \exp\left(\frac{A_0}{kT}\right)(N-1)\frac{4}{3}\,\pi\,(a_0^3 - b_0^3)\Big]\, J_{N-1}$$

$$= V\left[1 + \frac{(N-1)\,\delta}{V}\right] J_{N-1} \qquad (5.47)$$

where

$$\delta = -\frac{4}{3}\,\pi a_0^3 + \exp\left(\frac{A_0}{kT}\right)\frac{4}{3}\,\pi\,(a_0^3 - b_0^3)$$

$$= \frac{4}{3}\,\pi\,(a_0^3 - b_0^3)\left[\exp\left(\frac{A_0}{kT}\right) - 1\right] - \frac{4\pi}{3}\,b_0^3 \quad (5.48)$$

and J_{N-1} is a similar integral, but for the $(N-1)$-atom. Evaluating it in the same way, we find

$$J_{N-1} = V\left[1 + \frac{(N-2)\,\delta}{V}\right] J_{N-2}$$

It is now clear that the following expression holds for J_N

$$J_N = V^N\left[1 + \frac{(N-1)\,\delta}{V}\right]\left[1 + \frac{(N-2)\,\delta}{V}\right]\cdots\left[1 + \frac{\delta}{V}\right]$$

$$(5.49)$$

If we take logarithms of (5.49) and have in view that the probability of three or more atoms sticking together is low only at a small value of the ratio $(N-1)\,\delta/V$, we have

$$\ln\left[1 + \frac{(N-1)\,\delta}{V}\right] \approx \frac{(N-1)\,\delta}{V}$$

and similar expressions for the other terms, so that

$$\ln J_N = \ln (V^N) + \sum_{m=0}^{N-1} \ln \left(1 + \frac{m\delta}{V} \right) \approx \ln (V^N) + \sum_{m=0}^{N-1} \frac{m\delta}{V} \tag{5.50}$$

The last sum in (5.50) is the sum of N terms of an arithmetic progression, so that

$$\ln J_N = \ln (V^N) + \frac{N(N-1)\delta}{2V}$$

and, consequently,

$$J_N = V^N \exp \left[\frac{N(N-1)\delta}{2V} \right]$$

Hence,

$$Z = (2\pi m_0 kT)^{3N/2} V \exp \left[\frac{N(N-1)\delta}{2V} \right] \tag{5.51}$$

and the free energy of a real gas (calculated on the assumption that the "interaction volume" $N\delta$ in which forces of attraction manifest themselves is much smaller than the total volume occupied by the gas) is determined by the formula

$$F = -kT \ln Z = -kT \ln \Big\{ (2\pi m_0 kT)^{3N/2} V^N$$

$$\times \exp \left[\frac{N(N-1)\delta}{2V} \right] \Big\}$$

or

$$F = -kT N \left[\frac{3}{2} \ln T + \ln V + \frac{(N-1)\delta}{2V} + \ln (2\pi m_0 k)^{3/2} \right] \tag{5.52}$$

Expression (5.52) differs from formula (5.24) for the free energy of an ideal monatomic gas in the term with the ratio δ/V. For a gas consisting of polyatomic molecules, all the reasoning holds, and it is only necessary to substitute the term $(i/2) kT$ for $(3/2) kT$ (i is the number of degrees of freedom of a molecule).

Exercises

1. *Determine the magnitude of the fluctuations of the pointer in a balance having a sensitivity of* 10 mm *per milligram at* $T = 300$ K.
Solution. According to the equipartition theorem, the root-mean-square deviation is

$$\sqrt{\langle z^2 \rangle} = \sqrt{kT/\gamma}$$

where γ is the "rigidity" of the returning system. Since for a balance in equilibrium we have $mg = \gamma z$, then

$$\gamma = \frac{mg}{z} = \frac{10^{-6} \text{ kg} \times 9.81 \text{ ms}^{-2}}{10^{-2} \text{ m}} \approx 10^{-3} \text{ kg s}^{-2}$$

i.e. in the given case

$$\sqrt{\langle z^2 \rangle} = 2 \text{ nm}$$

The fluctuations have a value of the order of a score of interatomic distances.

2. *An amplifier has at its inlet a resonance circuit with a capacitance of* $C = 1000$ pF. *What is the limiting theoretical sensitivity of such an amplifier? Assume that* $T = 300$ K.

Solution. By formula (5.43), we have

$$\sqrt{\langle U^2 \rangle} = \sqrt{\frac{kT}{C}} = 2 \text{ } \mu\text{V}.$$

Chapter 6

RELATION OF STATISTICS TO THERMODYNAMICS

6.1. Equation of State

In addition to the statistical method, the **thermodynamic** approach is widely used in the physics of thermal phenomena. In this approach, conclusions are reached on particular properties of systems with the aid of a number of empirically established laws. It is quite natural that the statistical and the thermodynamic methods are close relatives. It is the object of the present chapter to show this relation. We shall begin with the **equation of state** of a system.

An equation of state is defined to be the dependence of the pressure P on the volume V and temperature T:

$$P = P (V, \, T) \tag{6.1}$$

For an ideal gas, the equation of state, known as the **Clapeyron-Mendeleev equation**, is well known and is written as

$$P = \frac{M}{\mu} \frac{RT}{V} \tag{6.2}$$

where M is the mass of the ideal gas, μ is its molar mass, and R is the molar gas constant.

Using the concept of free energy, we can obtain a general form of the equation of state that holds for any system, and not only for an ideal gas.

Assume that we have a vessel containing the system being considered, for instance a liquid or a non-ideal gas. Let the coordinate of one of the walls of the vessel perpendicular to the axis Ox have the value x. A graph showing how
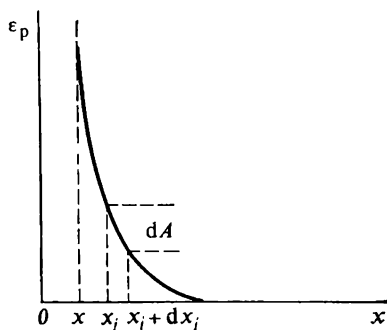
Fig. 6.1

the potential energy of one of the molecules of the system depends on the coordinate x has the form shown in Fig. 6.1. Indeed, the molecule i at the point x_i near the wall experiences from the latter a repulsive force equal to f'_i. The closer the molecule approaches the wall, the larger is the work that has to be done to overcome the repulsion and the higher is the potential energy of the molecule in the field of the repulsive force. Let us designate the potential energy of a molecule by ε_p. It is evident that ε_p depends only on the distance between the wall and the molecule, i.e.

$$\varepsilon_p = \varepsilon_p \, (x - x_i) \tag{6.3}$$

A glance at Fig. 6.1 shows that when the molecule travels from the point x_i to the point $x_i + dx_i$, and the repulsive force does the work

$$dA = f'_i \, dx_i \tag{6.4}$$

the potential energy diminishes, i.e. changes by the magnitude

$$d\varepsilon_p = \varepsilon_p(x_i) - \varepsilon_p(x_i + dx_i) = -\frac{d\varepsilon_p}{dx_i}\,dx_i \qquad (6.5)$$

A comparison of (6.4) and (6.5) shows that

$$f_i' = -\frac{d\varepsilon_p}{dx_i}$$

We shall be interested more in the force f_i with which the i-th molecule acts on the wall. Since by Newton's third law we have $f_i' = f_i$, then

$$f_i = \frac{d\varepsilon_p}{dx_i}$$

or, with a view to how the potential energy depends on the coordinates x and x_i by (6.3), we have

$$f_i = \frac{d\varepsilon_p}{dx_i} = -\frac{d\varepsilon_p}{dx} \qquad (6.6)$$

For the total force with which all the system's molecules act on the wall, we can write

$$F = \sum_{i=1}^{N} f_i = -\frac{d}{dx} \sum_{i=1}^{N} \varepsilon_p(x - x_i)$$

and for the mean value of this force

$$\langle F \rangle = \int \left[-\frac{d}{dx} \sum_{i=1}^{N} \varepsilon_p(x - x_i) \right] \exp\left(\frac{F - \mathscr{E}}{kT} \right) d\Gamma$$

The last expression is equivalent to the following one:

$$\langle F \rangle = -\int \frac{d\mathscr{E}}{dx} \exp\left(\frac{F - \mathscr{E}}{kT} \right) d\Gamma \qquad (6.7)$$

Indeed, the energy of the system is

$$\mathscr{E} = \sum_{i=1}^{N} \varepsilon_p(x - x_i) + \sum_{i=1}^{N} \frac{p_i^2}{2m_{0i}} + \mathscr{E}_{p,\,int} + \mathscr{E}_{p,\,ext} \qquad (6.8)$$

where the first term is the potential energy of interaction with the wall, the second is the kinetic energy of the molecules, and the remaining two terms are the potential energies

of interaction of the molecules with one another $\mathscr{E}_{\mathrm{p, int}}$ and with the field of the external forces $\mathscr{E}_{\mathrm{p, ext}}$, respectively. The last three terms do not depend on the coordinate x of the wall, so that after differentiation of (6.8), we obtain

$$\frac{\mathrm{d}\mathscr{E}}{\mathrm{d}x} = \frac{\mathrm{d}}{\mathrm{d}x} \sum_{i=1}^{N} \varepsilon_{\mathrm{p}} (x - x_i)$$

The pressure on the wall is the force acting on it related to unit area, hence

$$P = \frac{\langle F \rangle}{S} = -\int \frac{\mathrm{d}\mathscr{E}}{S\,\mathrm{d}x} \exp\left(\frac{F-\mathscr{E}}{kT}\right) \mathrm{d}\Gamma \qquad (6.9)$$

The product $S\,\mathrm{d}x$ equals the change in the volume of the system $\mathrm{d}V$ when the wall of the vessel is displaced by $\mathrm{d}x$. This allows us to write (6.9) in the form

$$P = -\int \frac{\mathrm{d}\mathscr{E}}{\mathrm{d}V} \exp\left(\frac{F-\mathscr{E}}{kT}\right) \mathrm{d}\Gamma \qquad (6.10)$$

It is simpler to evaluate the integral (6.10) proceeding from the normalization condition (5.13), which we shall write again:

$$1 = \int \exp\left(\frac{F-\mathscr{E}}{kT}\right) \mathrm{d}\Gamma \qquad (6.11)$$

Differentiating (6.11) with respect to the volume and taking into account that the energy $\mathscr{E}$ and the free energy F depend on the volume (on the coordinate of the wall), we find

$$0 = \int \exp\left(\frac{F-\mathscr{E}}{kT}\right) \frac{1}{kT} \left(\frac{\partial F}{\partial V} - \frac{\partial \mathscr{E}}{\partial V}\right) \mathrm{d}\Gamma$$

After cancelling $1/(kT)$, we can write the condition obtained in the form

$$\int \frac{\partial F}{\partial V} \exp\left(\frac{F-\mathscr{E}}{kT}\right) \mathrm{d}\Gamma = \int \frac{\partial \mathscr{E}}{\partial V} \exp\left(\frac{F-\mathscr{E}}{kT}\right) \mathrm{d}\Gamma$$

Since the free energy does not depend on the integration variables, we have

$$\int \frac{\partial F}{\partial V} \exp\left(\frac{F-\mathscr{E}}{kT}\right) \mathrm{d}\Gamma = \frac{\partial F}{\partial V} \int \exp\left(\frac{F-\mathscr{E}}{kT}\right) \mathrm{d}\Gamma = \frac{\partial E}{\partial V}$$

where the normalization condition (6.11) has been used. Consequently, *if the free energy is known as a function of the*

volume and temperature, the equation of state is written as follows:

$$P = -\frac{\partial F}{\partial V} \tag{6.12}$$

In Chap. 5, we determined the free energy of a monatomic ideal gas. By (5.24), it is

$$F = -kNT\left[\ln V + \frac{3}{2}\ln T + \ln(2\pi m_0 k)^{3/2}\right]$$

Using the basic relation (6.12), we find the equation of state:

$$P = \frac{kNT}{V}$$

If we take into account that the total number of molecules N is expressed in terms of the mass of a gas, its molar mass, and Avogadro's constant N_A, so that $N = N_A M/\mu$, we arrive at the Clapeyron-Mendeleev equation (6.2). We can find the equations of state for a liquid or a non-ideal gas in a similar way if we know their free energy.

6.2. Thermodynamic Meaning of the Free Energy

The free energy, formally derived above in terms of the partition function, has a physical meaning. To clarify it, let us consider a system in an isothermal process, i.e. at $T = \text{const}$. In the initial state, the free energy has one value corresponding to the initial volume, and in the final state it has another value corresponding to the final volume, but at the same temperature. With an infinitely small change in the volume, the change in the free energy is (we remember that $T = \text{const}$ and, therefore, $dT = 0$)

$$dF = \frac{\partial F}{\partial V}dV$$

With a view to (6.12), we can write this equation as follows:

$$dF = -P\,dV$$

Since we know that

$$P\,dV = dA$$

where dA is the work done by the system with an infinitely small expansion by dV, we find that $dF = -dA$. It is not

difficult to show by integration of the last equation that for finite isothermal expansions too, we have

$$\Delta F = -\Delta A \qquad (6.13)$$

The free energy belongs to the group of **state functions,** i.e. functions whose value is determined by the state of a system (the volume it occupies and its temperature) and does not depend on how the system arrived at this state. In this connection we can say that *the free energy F is a state function whose change in an isothermal process equals the work done by the system, but taken with the opposite sign.*

6.3. Gibbs-Helmholtz Equation

Differentiation of the normalization condition with respect to the volume yielded an important relation that resulted in an equation of state. Similarly, differentiation of the normalization condition with respect to the temperature yields an equally important equation known as the **Gibbs-Helmholtz equation.** Differentiation of (6.11) with respect to T gives

$$0 = \int \exp\left(\frac{F-\mathscr{E}}{kT}\right)\frac{\partial}{\partial T}\left(\frac{F-\mathscr{E}}{kT}\right)d\Gamma$$

$$= \int \exp\left(\frac{F-\mathscr{E}}{kT}\right)\left(\frac{1}{kT}\frac{\partial F}{\partial T}-\frac{F-\mathscr{E}}{kT^2}\right)d\Gamma$$

If we multiply both sides of the equation by kT^2 and represent the right-hand side as the sum of integrals, we have

$$0 = \int T\frac{\partial F}{\partial T}\exp\left(\frac{F-\mathscr{E}}{kT}\right)d\Gamma$$

$$- \int F\exp\left(\frac{F-\mathscr{E}}{kT}\right)d\Gamma + \int \mathscr{E}\exp\left(\frac{F-\mathscr{E}}{kT}\right)d\Gamma$$

Removing the factors $T\,(\partial F/\partial T)$ and F, which do not depend on the integration variables, from the integral and using the value of the normalization integral, we find

$$T\frac{\partial F}{\partial T}-F+\int \mathscr{E}\exp\left(\frac{F-\mathscr{E}}{kT}\right)d\Gamma = 0 \qquad (6.14)$$

The integral in (6.14) is the mean value of the energy of various states of a system. This quantity is called the **internal**

energy of the system and is designated by U, i.e.

$$U = \langle \mathscr{E} \rangle = \int \mathscr{E} \exp \left(\frac{F - \mathscr{E}}{kT} \right) d\Gamma$$

It therefore follows from (6.14) that

$$U = F - T \frac{\partial F}{\partial T} \tag{6.15}$$

Hence, *the internal energy is a state function equal to the mean value of the energy of a system, and its value can be determined in terms of the free energy with the aid of the Gibbs-Helmholtz equation* (6.15).

The Gibbs-Helmholtz equation holds for any system. Let us apply it as an example to a monatomic ideal gas. Introducing into (6.15) the free energy determined by expression (5.24), we find

$$U = F - T \frac{\partial F}{\partial T} = \frac{3}{2} kNT \tag{6.16}$$

or, in a different way,

$$U = \frac{3}{2} \frac{M}{\mu} N_A kT = \frac{3}{2} \frac{M}{\mu} RT \tag{6.16'}$$

6.4. Entropy and Its Thermodynamic Meaning

We can give the following definition: *the **entropy** S is defined to be a state function equal to*

$$S = - \frac{\partial F}{\partial T} \tag{6.17}$$

Since the free energy is a state function, it is natural that the quantities expressed in terms of it or its derivatives, i.e. the pressure, internal energy, and entropy, are also state functions. It is important, however, to determine the thermodynamic meaning of the new state function introduced in this way.

Let the state of a system change in a reversible process. We can consider the system to be in equilibrium at each stage of the reversible process, and therefore the Gibbs-Helmholtz equation holds. When the state of a system changes, its internal energy changes by ΔU, and by the

Gibbs-Helmholtz equation we have

$$\Delta U = \Delta F - \Delta \left(T \frac{\partial F}{\partial T} \right)$$

If the change is infinitely small, which corresponds to an infinitely small change in the volume dV and temperature dT, we obtain

$$dU = dF - d \left(T \frac{\partial F}{\partial T} \right) = \frac{\partial F}{\partial V} \, dV + \frac{\partial F}{\partial T} \, dT - \left(\frac{\partial F}{\partial T} \right) dT - Td \left(\frac{\partial F}{\partial T} \right)$$

$$(6.18)$$

The first term on the right-hand side can be written as

$$\frac{\partial F}{\partial V} \, dV = - P \, dV = - dA$$

where dA is the work done by the system. The second and third terms in (6.18) cancel each other. Finally, the last term in (6.18) by the definition of the entropy introduced above is

$$- T \, d \left(\frac{\partial F}{\partial T} \right) = T \, dS$$

Hence,

$$dU = -dA + T \, dS \qquad (6.19)$$

or

$$dS = \frac{dU + dA}{T} \qquad (6.20)$$

According to the first law of thermodynamics expressing the law of energy conservation with account taken of thermal phenomena, the sum of the change in the internal energy and in the work done by a system equals the amount of heat dQ supplied to the system in the process being considered. Hence,

$$dS = \frac{dQ}{T} \qquad (6.21)$$

Consequently, *the entropy is a state function of a system whose infinitely small change in a reversible process equals the ratio of an infinitely small amount of heat dQ added into the process to the temperature T at which it was added.*

For a finite reversible process, the change in the entropy can be evaluated by the formula

$$\Delta S = S_2 - S_1 = \int_1^2 dS = \int_1^2 \frac{dQ}{T} \qquad (6.22)$$

where the integral is taken from the initial state *1* of the system to its final state *2*. Since the entropy is a state function, a remarkable property of the integral (6.22) is its independence of the shape of the contour around which it is being evaluated.

Let us consider as an example of determining the entropy a monatomic ideal gas. Differentiating the free energy (5.24) with respect to the temperature, we find

$$S = kN \left[\ln V + \frac{3}{2} \ln T + \ln (2\pi m_0 k)^{3/2} \right] + \frac{3}{2} kN$$
$$= \frac{M}{\mu} R \left[\ln V + \frac{3}{2} \ln T + \ln (2\pi m_0 k e)^{3/2} \right]$$

where e is the base of natural logarithms (ln e = **1**).

6.5. Statistical Meaning of Entropy

The thermodynamic meaning of the entropy is abstract somewhat and does not allow us to understand why this state function plays such a major role in statistical physics and thermodynamics. The statistical meaning that can be put into this function is much more specific.

From the Gibbs-Helmholtz equation (6.15), we have

$$S = \frac{U - F}{T} \qquad (6.23)$$

Since

$$U = \int \mathscr{E} \exp\left(\frac{F - \mathscr{E}}{kT}\right) d\Gamma \quad \text{and} \quad F = \int F \exp\left(\frac{F - \mathscr{E}}{kT}\right) \Gamma$$

we can write

$$S = -k \frac{F - \langle \mathscr{E} \rangle}{kT} = -k \int \frac{F - \mathscr{E}}{kT} \exp\left(\frac{F - \mathscr{E}}{kT}\right) d\Gamma$$

The function

$$w = \exp\left(\frac{F - \mathscr{E}}{kT}\right)$$

is the probability density of the Gibbs distribution, so that the entropy is

$$S = -k \int w \ln w \, d\Gamma = -k \, \langle \ln w \rangle \qquad (6.24)$$

Formula (6.24) corresponds to the definition of the entropy as a measure of indefiniteness or chaos introduced in Sec. 2.6. A certain difference is due to the presence of the dimensional factor k, and also to the fact that in (2.23) we had to do with a discrete (countable) number of events and therefore performed summation, whereas in (6.24) we have to do with a continuous number, so that we had to replace summation with integration.

Hence, *the statistical meaning of the entropy consists in that it is a measure of the chaotic state of a system multiplied by the Boltzmann constant.*

We shall see on a later page that relation (6.24) plays a very important role in statistics and underlies the fundamental principle from which the entire statistics of equilibrium states can be sequentially derived. This principle is closely related to the second law of thermodynamics whose discussion will be started in the following section.

One of the variants of formula (6.24) is inscribed on the monument installed in the central cemetery of Vienna in honour of the eminent Austrian physicist Ludwig Boltzmann (1844-1906), who became famous for his works in the field of statistical physics.

6.6. Entropy and the Second Law of Thermodynamics

The second law together with the first one is the cornerstone of all thermodynamics and reflects the profound laws of phenomena observed in systems consisting of a very large number of microscopic particles. There are various equivalent statements of the second law. For instance, one of them states that *it is impossible to remove heat from a system and transform it completely into work without leaving other changes at the same time in the system or its surroundings.* If in the isothermal expansion of an ideal gas, work is done at the expense of the heat supplied from a heat bath, when the process terminates, the gas will occupy a larger volume,

i.e. changes will occur in comparison with the initial state. A gas or another working substance can be made to complete a closed reversible cycle, and the final state will coincide with the initial one. But here, according to the second law, not all the heat taken from a hot reservoir (heat source) will be converted into work; part of it must be fed at a lower temperature to a cold reservoir (heat sink). Hence follows a second statement: *a periodically operating heat engine that completely converts all the heat supplied to it into work (a perpetual motion machine of the second kind) is impossible.*

If a perpetual motion machine of the second kind were possible, we could obtain a certain amount of work by bringing it into contact with a cold reservoir. Using this work for actuating a reversible refrigerating machine, we would be able, by taking some more heat from the cold reservoir, to transfer it and the heat energy equal to the work obtained to the hot reservoir. It would thus be possible to take a certain amount of heat from the cooler body (the cold reservoir) and transfer it to the warmer body (the hot reservoir) so that after completion of the process, all the working substances would be in their initial condition. Since a perpetual motion machine of the second kind is impossible, the process indicated above is also impossible, i.e. *it is impossible to transfer heat from a cooler body to a warmer one without other changes occurring at the same time.*

It seems surprising at first sight that the statements given above are equivalent to a very simple and exact mathematical statement, namely: *in a reversible process, the quantity*

$$\frac{dQ}{T} \qquad (6.25)$$

is a total differential. In other words, upon a reversible transition from one state to another infinitely close one, expression (6.24) does not depend on the path (process) followed by the transition, but depends only on the initial and final states.

It was shown above that the following relation can be obtained from the Gibbs distribution

$$\frac{dQ}{T} = dS$$

where S is a state function, and, consequently, dS is a total differential, i.e. the second law of thermodynamics was

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proved in the last of the above statements. It only remains for us to establish how this last statement of the law leads to the preceding ones. Consider for this purpose a closed reversible process, for example, that shown in the P-V diagram in Fig. 6.2. The useful work obtained in this cycle is depicted by the hatched area in the figure:

$$A = \oint P \, dV$$

and equals the difference of the amount of heat Q_1 introduced into the system and the amount of heat $-Q_2$ given up
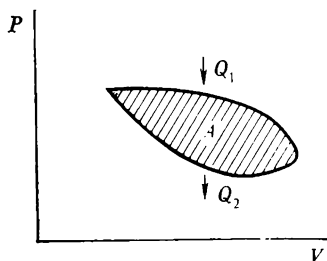

Fig. 6.2

by the system to the cold reservoir. The latter statement follows from the first law of thermodynamics. Since upon completion of a cycle, the system returns to its initial state, the change in its internal energy is zero. On the other hand, if we circumvent the cycle, then since the entropy is a state function, we must have

$$\oint dS = \oint \frac{dQ}{T} = 0 \qquad (6.26)$$

The temperature T is a positive quantity, hence if the integral is zero, we cannot have $dQ > 0$ all the time, i.e. a constant supply of heat to the system; there must be sections in which $dQ < 0$, i.e. where heat is given up. When work is done in a cycle, we have

$$A = Q_1 - Q_2 > 0$$

The condition (6.26) can be satisfied here only if heat is given up at a lower mean temperature T_2 than the mean temperature T_1 at which it is received so that at $Q_1 > Q_2$, we

have

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$

This proves the second statement or the first one equivalent to it.

To convince ourselves that the third statement is true, let us assume that there is a cold reservoir at the temperature T_2 lower than the temperature T_1 of the hot reservoir. Assume further that the heat Q_2 has been taken from the cold reservoir and $-Q_1$ has been transferred to the hot one. If there are no simultaneous changes in the system and the surroundings, the latter consequently do no work, and by the law of energy conservation, $Q_2 = Q_1$. But now, owing to the inequality of the temperatures, the equation

$$\oint \frac{\mathrm{d}Q}{T} = \frac{-Q_1}{T_1} + \frac{Q_2}{T_2} = 0$$

cannot be correct, so that the third statement is also true.

The second law of thermodynamics allows us to arrive at important conclusions on the efficiencies of heat engines. The efficiency of a machine is defined to be the ratio of the useful work done by it in a closed cycle to the amount of heat Q_1 taken by it from the hot reservoir:

$$\eta = \frac{A}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

The maximum efficiency is obtained at the largest ratio Q_1/Q_2 in the given conditions. If a machine is reversible, the condition

$$\oint \frac{\mathrm{d}Q}{T} = 0$$

must be observed, from which it follows that Q_1 can be larger when the temperature T_1 of the hot reservoir is higher, and Q_2 can be smaller when the temperature T_2 of the cold reservoir is lower. What has been said shows that of all the cycles having the same maximum temperature of the hot reservoir T_1° and the minimum temperature of the cold reservoir T_2°, the **Carnot cycle**, i.e. one consisting of two isothermal ($T_1 = \mathrm{const} = T_1^\circ$ and $T_2 = \mathrm{const} = T_2^\circ$) and two adiabatic processes, in which the transfer of heat is absent, has the largest efficiency.

Let us now determine the efficiency of a Carnot cycle, writing

$$\oint \frac{dQ}{T} = \int\limits_{T_1 = T_1^\circ} \frac{dQ}{T} + \int\limits_{T_2 = T_2^\circ} \frac{dQ}{T}$$

where the integrals over the adiabats have been omitted because $dQ = 0$ in an adiabatic process. Evaluation of the integrals over the isotherms leads to

$$\oint \frac{dQ}{T} = \frac{Q_1}{T_1} - \frac{Q_2}{T_2}$$

or

$$\frac{Q_2}{Q_1} = \frac{T_2}{T_1} \tag{6.27}$$

But according to the definition of the efficiency, we have

$$\eta = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

so that, with a view to (6.27), we find

$$\eta = 1 - \frac{T_2}{T_1} = \frac{T_1 - T_2}{T_1} \tag{6.28}$$

Hence, *the efficiency of a Carnot cycle is determined by relation (6.28) and does not depend on what working substance (gas, liquid) is used in performing this cycle.*

6.7. Real Gas

We shall use the relations obtained in the present chapter, and also the expression for the free energy of a real gas given in Sec. 5.7, for establishing some properties of a real gas.

By (5.52), the free energy has the form

$$F = -NkT \left[\frac{i}{2} \ln T + \ln V + \frac{N-1}{2} \frac{\delta}{V} + \ln (2\pi mk)^{3/2} \right] \tag{6.29}$$

where i is the number of degrees of freedom of the gas molecules.

An equation of state is readily obtained with the aid of (6.12). Indeed,

$$P = - \frac{\partial F}{\partial V} = NkT \left(\frac{1}{V} - \frac{N-1}{2} \frac{\delta}{V^2} \right) \tag{6.30}$$

Since the number of molecules $N = MN_A/\mu$, where M/μ is the number of moles (the amount of the substance), (6.30) can be rewritten as

$$P = \frac{M}{\mu} RT \left[\frac{1}{V} - \frac{N-1}{2} \frac{\delta}{V^2} \right]$$ (6.30')

At very large volumes, when $[(N - 1)/2]\,(\delta/V) \ll 1$, the equation of state of a real gas transforms into that of an ideal gas. At smaller volumes, a discrepancy is observed. Since Eq. (6.29) was derived from the very beginning assuming that $[(N - 1)/2]\,(\delta/V) < 1$, it is clear that we are speaking of relatively small differences of a real gas from an ideal one.

The pressure of a real gas at a given temperature and volume may be either larger or smaller than that of an ideal gas. Everything depends on the sign of the quantity $(N - 1)\,\delta/2$, which with a view to (5.48) is written as

$$\frac{(N-1)\delta}{2} = \frac{N-1}{2} \frac{4\pi}{3} (a_0^3 - b_0^3) \left[\exp\left(\frac{A_0}{kT} \right) - 1 \right] - \frac{N-1}{2} \frac{4\pi}{3} b_0^3$$ (6.31)

The negative part of this quantity has a simple physical meaning. Indeed, since b_0 is the diameter of a molecule, its volume is

$$\frac{4}{3} \pi \left(\frac{b_0}{2} \right)^3 = \frac{\pi}{6} b_0^3$$

The number of molecules in a gas is very large, and we may therefore assume that $N - 1 \approx N$. The negative term can be seen now to equal the quadruple volume of all the molecules.

The positive term is interpreted in a somewhat more complicated way. We must note that at $A_0 \ll kT$ it becomes simplified because here we have

$$\exp\left(\frac{A_0}{kT} \right) - 1 \approx \frac{A_0}{kT}$$ (6.32)

The factor

$$\frac{N-1}{2} \frac{4}{3} \pi (a_0^3 - b_0^3)$$

has the meaning of half the volume in which the attraction of the molecules tells.

Let us compare the equation of state (6.30) with the van der Waals equation known from the general course of physics, which is often used to describe the state of real gases and their transition to the liquid state. This equation is

$$\left(P + \frac{M^2}{\mu^2} \frac{a}{V^2} \right) \left(V - \frac{M}{\mu} b \right) = RT \frac{M}{\mu}$$

or

$$P = \frac{(M/\mu) RT}{V - (M/\mu) b} - \frac{M^2}{\mu^2} \frac{a}{V^2}$$

If we limit ourselves to volumes $V \gg bM/\mu$, we obtain the following approximate expression to within first-order terms with respect to $bM/\mu V$:

$$P = \frac{M}{\mu} \frac{RT}{V} + \frac{M^2}{\mu^2} \frac{RT}{V^2} b - \frac{M^2}{\mu^2} \frac{a}{V^2} \qquad (6.33)$$

This equation coincides with the theoretical equation (6.30) obtained above, which with account taken of (6.31) can be written as follows:

$$P = \frac{M}{\mu} \frac{RT}{V} + \frac{M}{\mu} \frac{RT}{V^2} \frac{N-1}{2} \frac{4}{3} \pi b_0^3$$

$$- \frac{M}{\mu} \frac{RT}{V^2} \frac{N-1}{2} (a_0^3 - b_0^3) \frac{4}{3} \pi \frac{A_0}{kT} \qquad (6.34)$$

A comparison of Eqs. (6.34) and (6.33) shows that they coincide if

$$b = \frac{\mu}{M} \frac{N-1}{2} \frac{4}{3} \pi b_0^3 \approx \frac{N_A}{2} \frac{4}{3} \pi b_0^3 \qquad (6.35)$$

i.e. if b is the quadruple volume of all the molecules contained in one mole, and if

$$a = \frac{\mu}{M} \frac{R}{k} \frac{N-1}{2} \frac{4}{3} \pi (a_0^3 - b_0^3) A_0$$

$$\approx \frac{N_A}{2} \frac{R}{k} \frac{4}{3} \pi (a_0^3 - b_0^3) A_0 = \frac{N_A^2}{2} \frac{4}{3} \pi (a_0^3 - b_0^3) A_0 \quad (6.36)$$

Hence, *the statistical method leads to an equation of state that for large volumes coincides with the van der Waals equation and allows us to express the constants a and b of this equation in terms of parameters characterizing the molecules* (a_0, b_0, A_0). We must note that in principle, the expression for the free energy could be derived more precisely, and the

result would be a more accurate equation of state. A treatment of these matters, however, is beyond the scope of the present text.

Let us now evaluate the internal energy of a real gas. By the Gibbs-Helmholtz equation (6.15) with the aid of (6.29), we obtain

$$U = \frac{i}{2} NkT + NkT^2 \frac{1}{V} \frac{\partial}{\partial T} \left[\frac{N-1}{2} \delta \right]$$

$$= \frac{M}{\mu} \frac{i}{2} RT + \frac{M}{\mu} T^2 \frac{R}{V} \frac{\partial}{\partial T} \left[\frac{N-1}{2} \delta \right] \qquad (6.37)$$

Since the expression for $\delta (N-1)/2$ with a view to relations (6.35) and (6.36) in the approximation stipulated by the condition (6.32) can be written as

$$\frac{\delta (N-1)}{2} = \frac{M}{\mu} \left(\frac{a}{RT} - b \right) \qquad (6.38)$$

we obtain

$$\frac{\partial}{\partial T} \left[\frac{N-1}{2} \delta \right] = \frac{\partial}{\partial T} \left[\frac{M}{\mu} \left(\frac{a}{RT} - b \right) \right] = - \frac{M}{\mu} \frac{a}{RT^2}$$

Hence, the internal energy is

$$U = \frac{M}{\mu} \frac{i}{2} RT - \left(\frac{M}{\mu} \right)^2 \frac{a}{V} \qquad (6.39)$$

A glance at (6.39) shows that the internal energy of a real gas differs from that of an ideal one in the term $-(M/\mu)^2(a/V)$ that takes into account the potential energy of mutual attraction of the molecules. The internal energy depends on the volume occupied by a gas.

Using Eq. (6.17), we can readily calculate the entropy of a real gas. With account taken of (6.38), we have

$$S = - \frac{\partial F}{\partial T} = Nk \left[\frac{i}{2} \ln T + \ln V - \frac{M}{\mu} \frac{b}{V} + \frac{M}{\mu} \frac{a}{VRT} \right.$$

$$\left. + \ln (2\pi mk)^{3/2} \right] + \frac{i}{2} Nk - Nk \left(\frac{M}{\mu} \right) \frac{a}{VRT}$$

Since $Nk = MR/\mu$, we have

$$S = \frac{M}{\mu} R \left[\frac{i}{2} \ln T - \ln V - \frac{M}{\mu} \frac{b}{V} \right] + \text{const} \qquad (6.40)$$

The entropy of a real gas is somewhat smaller than that of an ideal one owing to the presence of forces of repulsion.

This leads to a difference in the relation between the temperature and the volume in an adiabatic process from the one for an ideal gas under the same conditions. This matter is considered in greater detail in Example 3 to the present chapter.

6.8. Heat Capacity

The **heat capacity** is defined to be a quantity numerically equal to the amount of heat that must be added to a system to heat it by one kelvin:

$$C = \frac{\mathrm{d}Q}{\mathrm{d}T} \tag{6.41}$$

In gases, whose compressibility is very great, we must distinguish between the heat capacity at constant volume C_V and the heat capacity at constant pressure C_P. In condensed systems (liquids and solids), the change in volume when a pressure is applied is so small, as a rule, that the difference between C_V and C_P may be disregarded.

Since by the first law of thermodynamics, we have

$$\mathrm{d}Q = \mathrm{d}U + \mathrm{d}A = \mathrm{d}U + P\,\mathrm{d}V \tag{6.42}$$

for the heat capacity, we obtain

$$C = \frac{\mathrm{d}U}{\mathrm{d}T} + P\,\frac{\mathrm{d}V}{\mathrm{d}T}$$

At constant volume, $\mathrm{d}V/\mathrm{d}T = 0$, and, therefore,

$$C_V = \frac{\mathrm{d}U}{\mathrm{d}T} \tag{6.43}$$

Relation (6.43) explains why the heat capacity is of great practical interest. It is relatively simple to measure, and for this reason it can be used for the experimental determination of the internal energy of a system. If the temperature is increased and the pressure is constant, the volume of the system increases, and this is why the heat capacity at constant pressure is larger than that at constant volume:

$$C_P = \frac{\mathrm{d}U}{\mathrm{d}T} + P\,\frac{\mathrm{d}V}{\mathrm{d}T} = C_V + P\,\frac{\mathrm{d}V}{\mathrm{d}T} \tag{6.44}$$

We very often have to do with the **specific heat capacity** (sometimes called the specific heat), i.e. the heat capacity

divided by the mass:

$$c_V = \frac{C_V}{M}, \quad c_P = \frac{C_P}{M} \tag{6.45}$$

Sometimes the **molar heat capacity** (the heat capacity of one mole) is used:

$$c_{m, V} = \frac{C_V \mu}{M}, \quad c_{m, P} = \frac{C_P \mu}{M} \tag{6.46}$$

Let us now turn to the heat capacity of an ideal gas. If we use relation (5.33) for the internal energy of an ideal gas, the heat capacity at constant volume is determined by the formula

$$C_V = \frac{M}{\mu} \frac{i}{2} R \tag{6.47}$$

or for the molar heat capacity

$$c_{m, V} = \frac{i}{2} R \tag{6.48}$$

For a constant pressure, it follows from (6.44) that

$$C_P = C_V + P \frac{dV}{dT} = C_V + \frac{d}{dT}(PV) = C_V + \frac{d}{dT}\left(\frac{M}{\mu} RT\right)$$

$$= C_V + \frac{M}{\mu} R \tag{6.49}$$

Here the Clapeyron-Mendeleev equation has been used. With a view to (6.47), Eq. (6.49) can also be written as

$$C_P = \frac{M}{\mu} \frac{i+2}{2} R \tag{6.50}$$

For the molar heat capacity at constant pressure, it follows from (6.49) that

$$c_{m, P} = c_{m,V} + R \tag{6.51}$$

This important equation presented by J. Mayer played a great role in the history of physics in establishing the law of energy conservation and determining the mechanical equivalent of heat.

Heat capacities are convenient quantities for verifying the agreement of theory and practice. Experiments show that relations (6.47)-(6.50) are observed very well in a number of cases and thus seem to confirm the correctness of theory. As

we already indicated in Sec. 5.5, however, the conclusions of the classical theory actually contradict experimental results. If, for example, account were taken of the degrees of freedom relating to individual electrons, the total number of degrees of freedom i of an atom would be considerably larger than was assumed before. The degrees of freedom relating to the electrons ought to contribute to the heat capacity too, so that the result would be much larger than the value actually observed experimentally.

Hence, *part of the degrees of freedom for reasons unknown in classical statistics must not be taken into account*. This is also supported by the circumstance that in cooling, some gases, for example hydrogen, even before condensation exhibit a decrease in their heat capacity, which can be explained only by presuming that the number of degrees of freedom changes and instead of five gradually becomes equal to three. This effect is spoken about as of a case when the rotational degrees of freedom "freeze out". On the other hand, only for the relatively simple polyatomic molecules such as water H_2O or methane CH_4 does the number of degrees of freedom equal six. For more complicated molecules, for instance ethyl alcohol C_2H_5OH, the heat capacity is larger than the value corresponding to an ideal gas with six degrees of freedom. This fact is not surprising by itself and only signifies that the degrees of freedom must be considered that take the possibility of relative motion of the atoms in a molecule into consideration. An attempt to take account of these degrees of freedom quantitatively within the scope of classical statistics cannot result in agreement with experimental data. Along general lines, this is explained as follows.

The motion of atoms relative to one another at the small displacements that usually occur in a molecule can be described with adequate accuracy by considering that the atoms are bound by quasi-elastic forces. Therefore, the energy $kT/2$ corresponding to the kinetic energy and $kT/2$ corresponding to the potential energy falls to each degree of freedom. The total mean energy is thus proportional to the temperature, whence it follows that the heat capacity at constant volume is constant. Experiments convincingly show that this is not true, and that the heat capacity increases with elevation of the temperature.

These paradoxes of classical statistical physics were explained only when the quantum effects were taken into consideration.

Exercises

1. *Proceeding from the expression for the free energy of an ideal monatomic gas, find the work it does in an isothermal process when expanding from V_1 to V_2.*

Solution. According to the thermodynamic meaning of the free energy, we have

$$A = F_1 - F_2$$

Using expression (5.24), we obtain

$$A = -RT \frac{M}{\mu} \left[\ln V_1 + \frac{3}{2} \ln T + \ln (2\pi m_0 ke)^{3/2} \right]$$

$$+ RT \frac{M}{\mu} \left[\ln V_2 + \frac{3}{2} \ln T + \ln (2\pi m_0 ke)^{3/2} \right] = RT \frac{M}{\mu} \ln \left(\frac{V_2}{V_1} \right)$$

2. *Proceeding from the expression for the entropy of an ideal monatomic gas, find the relation between the temperature and the volume in an adiabatic process.*

Solution. The entropy does not change in an adiabatic process, hence,

$$0 = S_1 - S_2 = \frac{M}{\mu} R \left[\ln V_1 + \frac{3}{2} \ln T_1 + \ln (2\pi m_0 ke)^{3/2} \right]$$

$$- \frac{M}{\mu} R \left[\ln V_2 + \frac{3}{2} \ln T_2 + \ln (2\pi m_0 ke)^{3/2} \right]$$

or

$$\ln V_1 + \frac{3}{2} \ln T_1 = \ln V_2 + \frac{3}{2} \ln T_2$$

that is

$$V_1 T_1^{3/2} = V_2 T_2^{3/2}$$

3. *Find the relation between the temperature and the volume in an adiabatic process for a real gas.*

Solution. From the condition of the process being adiabatic, we have $S = $ const, and with the aid of (6.40), we find

$$\frac{i}{2} \ln T + \ln V - \frac{M}{\mu} \frac{b}{V} = \text{const}$$

or, after taking antilogarithms,

$$T^{i/2} V \exp \left(-\frac{M}{\mu} \frac{b}{V} \right) = \text{const}$$

Since by assumption $Mb/(\mu V) \ll 1$, we limit ourselves to the first two terms of the expansion of the exponential into a series, and can write

$$T^{i/2}V \left(1 - \frac{M}{\mu} \frac{b}{V} \right) = \text{const}$$

or, finally,

$$T^{i/2} \left(V - \frac{M}{\mu} b \right) = \text{const}$$

Hence, in accordance with the van der Waals equation, the gas behaves as if its free volume is less than the volume of the vessel by the quad ruple volume of all the molecules in it.

Part III

QUANTUM STATISTICS
OF EQUILIBRIUM STATES

Chapter 7

SOME INFORMATION FROM
QUANTUM MECHANICS

7.1. The Quantum Properties of Radiation

By the end of the 19th century, it was established that light has an electromagnetic wave nature. At the beginning of the 20th century, however, it was discovered that the explanation of a number of phenomena also makes it necessary to involve a notion of quasi-particles of light—**photons**. The quantum properties of electromagnetic radiation are exhibited when it interacts with a substance (in absorption, radiation, etc.) and consist in that energy and momentum are transferred from a wave to a substance in finite portions. For example, the energy of light of a definite frequency ν (a definite wavelength λ) is absorbed and emitted in portions—quanta, whose energy is determined by the formula

$$\varepsilon = h\nu = 2\pi\hbar\nu \qquad (7.1)$$

where $h = 6.626 \times 10^{-34}$ J·s $= 6.626 \times 10^{-27}$ erg·s is the Planck constant, and $\hbar = h/2\pi = 1.055 \times 10^{-34}$ J·s $= 1.055 \times 10^{-27}$ erg·s. The first to realize the necessity of introducing the notion of quanta was M. Planck when working on the theory of blackbody radiation. This notion was later confirmed in many other optical effects such as the photoelectric effect and the radiation of atoms and molecules.

By the known relation presented by A. Einstein, which we already used in Chap. 5, the energy is related to the

mass:

$$\varepsilon = mc^2 \qquad (7.2)$$

Hence, if we compare the notion of a light particle called a photon with a quantum of light energy, then since the speed of propagation of light is c, the momentum of a photon is

$$p = mc = \frac{\varepsilon}{c}$$

Introducing into this expression the energy of a photon according to (7.1), we obtain

$$p = \frac{2\pi\hbar\nu}{c} = \frac{2\pi\hbar}{\lambda} = k\hbar \qquad (7.3)$$

where

$$k = \frac{2\pi}{\lambda} \qquad (7.4)$$

is the **wave number** of a photon.

We must note that *the quantum properties of radiation manifest themselves not so much in that electromagnetic waves must be treated as a flux of particles—photons, as in taking account of the fact that a wave exchanges finite portions of energy and momentum with a substance in accordance with formulas* (7.1) *and* (7.3).

7.2. Wave Properties of Particles

Numerous experimental facts convince us that not only waves, particularly light, have corpuscular properties, but, conversely, particles have wave properties too. The most striking confirmation of this proposition, which was first advanced by L. de Broglie in 1923, is probably the diffraction of electrons.

It is known that when waves pass through a diaphragm (slit), the alternation of maxima and minima of intensity in the form of fringes is observed beyond a converging lens on a screen at a distance from the slit. All the bright fringes except the central one are in the region of the geometric shadow.

Assume that a plane monochromatic light wave is incident on a slit normal to it, i.e. along the direction chosen as that of the z-axis. The electric field strength vector **E** in this

wave is described by the expression

$$\mathbf{E} = \mathbf{E}_0 \cos (\omega t - kz)$$

where $\mathbf{E}_0$ is the amplitude of the field strength vector, $\omega = 2\pi\nu$ is the angular or cyclic frequency, and $k = 2\pi/\lambda$ is the wave number.

The equation of a wave can also be written in the complex form:

$$\mathbf{E} = \mathbf{E}_0 e^{-i(\omega t - kz)}$$

The theory of diffraction tells us that the direction φ of the first minimum of the diffraction pattern is determined by the relation

$$\sin \varphi = \frac{\lambda}{a} \tag{7.5}$$

where a is the width of the slit. This relation can be explained as follows. The ray *2* passing through the middle
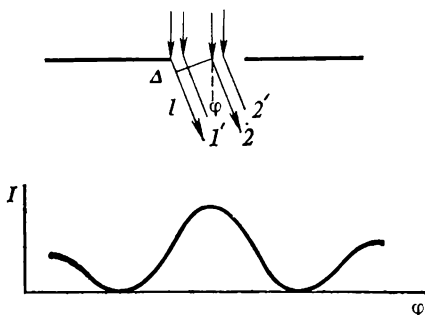

Fig. 7.1

of the slit (Fig. 7.1) after diffraction in the direction φ has the path difference

$$\Delta = \frac{a}{2} \sin \varphi$$

with respect to the ray *1* passing through the edge of the slit. If the condition (7.5) is satisfied, the path difference Δ leads to a phase shift of π between the rays. Consequently, when the rays reach the screen, they interfere destructively. It is not difficult to see that all the rays can be divided into pairs interfering destructively if the direction φ satisfies the condition (7.5). Indeed, the ray *1'* (Fig. 7.1) can be

associated with the ray *2'* travelling at the same distance from the ray *2* at which the ray *1'* is from the ray *1*. The phase difference between them is also π. Hence, all the rays interfere destructively, and the direction φ does indeed correspond to the minimum intensity. The bottom portion of Fig. 7.1 shows how the light intensity is distributed on the screen depending on the angle φ.

The intensity is distributed differently for diffraction by two slits; it does not coincide with the sum of the intensities observed for each of the slits separately.

In experiments conducted by C. Davisson and L. Germer (1927), it was discovered that electrons reflected from crystals also experience diffraction. In 1949 in experiments run by V. Fabrikant, N. Sushkin, and L. Biberman, diffraction was observed at such a low intensity of the electron flux that interaction between the electrons was excluded, and each electron diffracted independently. The phenomenon of electron diffraction sharply contradicts our conventional notion of them as of classical particles. This contradiction manifests itself especially strikingly in interpreting the diffraction experiment using two slits. That the diffraction pattern with two slits differs from the one obtained using one slit is associated with the passing of the wave through both slits simultaneously and with the interference of these two wave portions. From the viewpoint of classical notions, an electron-particle passes either through one slit or through the other one and it is absolutely incomprehensible why when passing through one slit it is affected by the presence of the adjacent one through which it has not passed.

To explain this and many other effects, physicists found it necessary to renounce classical mechanics and go over to quantum or wave mechanics. When taking wave properties into consideration, a wave is associated with each particle, particularly with each electron. If we limit ourselves to particles that are in an infinitely deep potential well of a sufficiently large volume V, we can associate with each particle a de Broglie wave having the form

$$\Psi = \frac{1}{\sqrt{V}}\, e^{-i(\omega t - \mathbf{k}\mathbf{r})} \tag{7.6}$$

The frequency ω of a wave and its wave vector $\mathbf{k}$ are obtained from formulas (7.1) and (7.3) that determine the **corpuscular**

properties of waves. We thus have

$$\omega = \frac{\varepsilon}{\hbar} \tag{7.7}$$

and

$$\mathbf{k} = \frac{\mathbf{p}}{\hbar} \tag{7.8}$$

where ε is the energy of a particle, and $\mathbf{p}$ is its momentum. The physical meaning of the Ψ-wave describing the behaviour of a particle consists in that the quantity

$$dW = |\Psi(\mathbf{r}, t)|^2 \, d\tau \tag{7.9}$$

equals the probability of detecting the particle in the volume $d\tau$ in the vicinity of a point with the position vector $\mathbf{r}$ at the instant t. Using (7.9) and (7.6), we find for a particle in a potential well that

$$dW = \frac{d\tau}{V}$$

i.e. the probabilities of the particle being at any point are the same.

The explanation of the diffraction experiment consists in that when the de Broglie wave of a free electron is incident on a slit, it experiences diffraction, and in some directions its intensity (i.e. the probability of detecting the electron) is maximum, while in others it is minimum.

Hence, *particles have wave properties, and to describe them it is necessary, particularly, to associate with each particle in an infinitely deep potential well of the large volume V a de Broglie wave (7.6) having a frequency and wave vector determined by formulas (7.7) and (7.8).*

7.3. Quantization of Radiation

Electromagnetic radiation exists in a cavity with ideally conducting walls (a metal cavity) in the form of standing waves of definite frequencies. The frequency of a wave is determined from the condition that there must be a node of the electric field on the boundary with the wall (the electric field vanishes) because otherwise a large current flows in the wall and the wave rapidly attenuates owing to the Joule (heat) loss.

Assume, for instance, that we have a rectangular metal container with the sides a, b, and c chosen as the directions x, y, and z of a Cartesian system of coordinates, respectively (Fig. 7.2). If a running wave of the strength

$$E_1 = E_0 \exp\left[-i\left(\omega t - k_x x\right)\right]$$
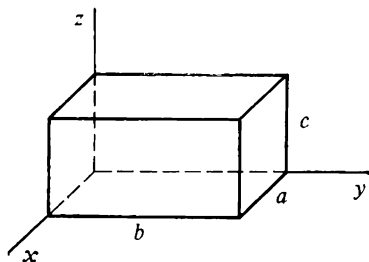
propagates along the x-axis, upon reflection from the con-

Fig. 7.2

tainer wall, it gives birth to the opposite running wave

$$E_2 = E_0 \exp\left[\left(-i\left(\omega t + k_x x + \alpha\right)\right)\right]$$

where α is the angle characterizing the phase shift in reflection. The interference of E_1 and E_2 produces the standing wave

$$E = E_1 + E_2 = E_0 \exp\left(-i\omega t\right)\left[\exp\left(ik_x x\right) + \exp\left(-ik_x x - i\alpha\right)\right]$$

$$= 2E_0 \exp\left(-i\omega t\right) \exp\left(-\frac{i\alpha}{2}\right) \cos\left(k_x x + \frac{\alpha}{2}\right)$$

Let the origin of coordinates be chosen so that the first wall perpendicular to the x-axis is at $x = 0$, and the second is at $x = a$. Here the following conditions must hold:

$$E|_{x=0} = 2E_0 \exp\left(-i\omega t\right) \exp\left(-\frac{i\alpha}{2}\right) \cos\frac{\alpha}{2} = 0 \quad (7.10)$$

$$E|_{x=a} = 2E_0 \exp\left(-i\omega t\right) \exp\left(-\frac{i\alpha}{2}\right) \cos\left(k_x a + \frac{\alpha}{2}\right) = 0 \quad (7.11)$$

Equation (7.10) gives us the angle α. Since $\cos(\alpha/2) = 0$, we obtain $\alpha = \pi$. The condition (7.11) leads to the equation

$$\cos\left(k_x a + \frac{\pi}{2}\right) = -\sin\left(k_x a\right) = 0$$

that is,

$$k_x = \frac{\pi}{a} \, m_x \qquad (7.12)$$

where m_x is an arbitrary integer, $m_x = 1, 2, \ldots$. Consequently, not any values of the wave number k_x are possible, but only those that satisfy the condition (7.12). Using the relation of the wave number to the wavelength, we find that only those wavelengths are possible which satisfy the relation

$$m_x \frac{\lambda}{2} = a$$

i.e. an integral number of half-waves must be accommodated along the length of the container wall.

Similarly, if the running wave propagates along the y-axis, a standing wave sets in for which

$$k_y = \frac{\pi}{b} \, m_y \qquad (7.13)$$

where m_y also takes on arbitrary integral values $m_y = 1, 2, \ldots$. The same holds for a wave directed along the z-axis:

$$k_z = \frac{\pi}{c} \, m_z \qquad (7.14)$$

$(m_z = 1, 2, \ldots)$. Finally, in the general case when a wave propagates in an arbitrary direction characterized by the wave vector **k** with the components $\{k_x, k_y, k_z\}$, a standing wave is set up for which the components of the wave vector satisfy all three conditions (7.12), (7.13), and (7.14). Since the wavelength is related to the wave vector by the expression $2\pi/\lambda = |\mathbf{k}|$, we obtain the following result for the possible wavelengths:

$$\lambda = 2 \left(\sqrt{\frac{m_x^2}{a^2} + \frac{m_y^2}{b^2} + \frac{m_z^2}{c^2}} \right)^{-1} \qquad (7.15)$$

For a number of reasons, it is more convenient to deal not with standing, but with running waves, for which, particularly, the important equations (7.1) and (7.3) hold.

Although each standing wave consists of two running ones that propagate towards each other, the amplitudes of these waves are equal, so that they cannot be considered as independent. Hence, the number of pairs of running waves equals the number of possible standing ones. It would be convenient to consider the amplitudes of the running waves independent of each other, but in this case the number of independent variables describing the electromagnetic oscillations in the container, i.e. of the amplitudes E_0 corresponding to each value of the vector $\mathbf{k}$ would be double what it should be. The following way out is used. It is assumed that a whole number of wavelengths is accommodated along the length of a container wall instead of a whole number of half-waves, as is actually what occurs, i.e. the following relations are used instead of (7.12), (7.13), and (7.14):

$$k_x = \frac{2\pi}{a}\, m_x, \quad k_y = \frac{2\pi}{b}\, m_y, \quad k_z = \frac{2\pi}{c}\, m_z \qquad (7.16)$$

Consequently, the number of possible wavelengths has been halved, but now we may consider the amplitudes of the running waves corresponding to them to be independent because a proper number of independent variables is retained. In essence, in this method, two standing waves with close λ's relating to two values of $\mathbf{k}$ [for example, $k_x = (\pi/a)\, 2m_x$, $k_y = 0$, $k_z = 0$, and $k_x = (\pi/a)\, (2m_x + 1)$, $k_y = 0$, $k_z = 0$] are replaced with two waves running in opposite directions with the same value of $\mathbf{k}$ [$k_x = (2\pi/a)\, m_x$, $k_y = 0$, $k_z = 0$], but with independent amplitudes. If the walls of the container are much greater than the length of the waves we are interested in, such a substitution will not lead to a large error. In the long run, we are interested in radiation in unlimited space. Consequently, in the final results we must perform a limiting process with the walls a, b, and c expanding to infinity. Now the transition from standing waves to running ones will hold not approximately, but exactly.

It is evident from the above that an electromagnetic wave existing in a container can be represented as a sum, generally speaking, as an infinite one, of standing waves of definite frequencies. If the container is large enough, the field reduces to the sum of running waves. Since the frequency of electromagnetic oscillations is related to the wavelength by the expression $\omega = 2\pi c/\lambda = |\mathbf{k}|\, c$, with a view to (7.15),

frequencies of the running waves are possible that are determined by the formula

$$\omega = 2\pi c \sqrt{\frac{m_x^2}{a^2} + \frac{m_y^2}{b^2} + \frac{m_z^2}{c^2}} \qquad (7.17)$$

From the mathematical viewpoint, the above result is a corollary of the Fourier theorem and is correct in both the classical and the quantum theory.

Let us now turn to what is new that follows from quantum mechanics. Since the energy of a monochromatic running wave is transmitted in discrete portions—quanta, we must conclude that the total energy of a wave consists of a certain integral number of such quanta, i.e.

$$\varepsilon = 2\pi\hbar\nu n = \hbar\omega n \qquad (7.18)$$

where $n = 1, 2, \ldots$. Strictly speaking, (7.18) relates only to the part of the energy that can be taken from or transmitted to the wave, and we can assume that there is some more energy ε_0 which is associated with the wave, but does not participate in exchange. For simplicity, we shall drop ε_0 in the following, so that (7.18) determines the total energy.

Since the energy of an individual monochromatic wave, in accordance with (7.18), takes on discrete values, and all the other values of the energy are impossible, this signifies that according to the quantum theory the amplitude of a plane wave is not arbitrary, but must have a value satisfying Eq. (7.18). The numbers m_x, m_y, m_z determining the wave vector **k** are known as the **quantum numbers** of the running wave. Assume that these numbers take on specific values $m_{x\alpha}$, $m_{y\alpha}$, and $m_{z\alpha}$, for instance $m_{x\alpha} = 2$, $m_{y\alpha} = 5$, and $m_{z\alpha} = 3$. Here the frequencies ω_α that are calculated by formula (7.17) correspond to them. The energy ε_α of a plane wave with this frequency can have a value determined by formula (7.18) at $\omega = \omega_\alpha$ and a certain value of the number n that we shall designate by n_α, i.e.

$$\varepsilon_\alpha = \hbar\omega_\alpha n_\alpha$$

Consequently, *a running wave, to which we assign the subscript* α, *is set by three quantum numbers* $m_{x\alpha}$, $m_{y\alpha}$, *and* $m_{z\alpha}$ *that define its wave vector, and by the number* n_α *called the* **occupation number**, *that sets its energy (amplitude)*. The same result

can be interpreted if we proceed from the notion of corpuscles (particles) of radiation—photons. From the latter viewpoint, each running wave is a collection of photons. Each photon has the momentum **p**, which by formulas (7.8) and (7.11) has the components

$$
\left.
\begin{aligned}
p_{x\alpha} &= \hbar k_{x\alpha} = \hbar \, \frac{2\pi}{a} \, m_{x\alpha} \\[4pt]
p_{y\alpha} &= \hbar k_{y\alpha} = \hbar \, \frac{2\pi}{b} \, m_{y\alpha} \\[4pt]
p_{z\alpha} &= \hbar k_{z\alpha} = \hbar \, \frac{2\pi}{c} \, m_{z\alpha}
\end{aligned}
\right\}
\qquad (7.19)
$$

7.4. Indistinguishability

The representation of a running wave in the form of a certain number of quanta has an important feature that can easily be explained with the help of the following example.

Assume that water is poured into a vessel or scooped out of it with the aid of a dipper that is always filled to the same level. It is evident that the total amount of water is an integral number of dipper volumes, i.e. we can say that the vessel contains n (where n is an integer) dippers, or "particles" of water. In scooping out the water, we can extract one, two, or even all the n "particles". The particles of water, however, differ in one respect from the conventional classical particles. Indeed, although our vessel contains n particles, they are impersonal, i.e. they cannot be numbered so that in scooping them out we could assert that we have extracted a particle with a given number, for example, the third one. Hence, *in speaking of photons as of particles, we must have in view that they are **indistinguishable** from one another.*

The indistinguishability of particles has a substantial significance in a variety of statistical applications. To explain what matters are here, let us first consider a vessel with real particles, for example, balls. If we shake our vessel, the ⸏ lls will change their positions so that although their total n mber does not change, we nevertheless obtain a new state because some of the balls changed places with other ones. In shaking a vessel with water, we cannot speak of a new state because the division of the water itself into "particles" is conditional.

7.5. Number of States of a Quantum Particle in a Volume Element of μ-Space

Our notion of photons allows us to consider them in a cavity as an ideal gas of quantum particles in a closed volume. Now we shall take into account that not any states of a photon are possible. Indeed, the momentum of a classical particle confined in an infinitely deep potential well may have any value, whereas a photon can have only values of the momentum corresponding to formulas (7.18). This difference becomes
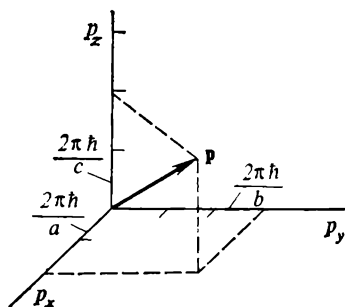

Fig. 7.3

clearer when considering momentum space. For classical particles, any vector in this space determines the possible values of the momentum, whereas for photons by (7.19) there may only be vectors whose components along the axes are integers, multiples of the same quantities, namely, $2\pi\hbar/a$ for the p_x-axis, $2\pi\hbar/b$ for the p_y-axis, and $2\pi\hbar/c$ for the p_z-axis (Fig. 7.3). Hence, the tips of the momentum vectors of a photon form a rectangular lattice in momentum space. To each vector of the lattice, i.e. to each of its points, there corresponds an elementary parallelepiped with the volume

$$\Delta\Omega = \Delta p_x \, \Delta p_y \, \Delta p_z = \frac{2\pi\hbar}{a} \frac{2\pi\hbar}{b} \frac{2\pi\hbar}{c} = \frac{(2\pi\hbar)^3}{V} \quad (7.20)$$

Although the volume $\Delta\Omega$ is finite, it is very small from the viewpoint of our conventional macroscopic notions. For example, in a cubic space with a dimension of $a = 1$ cm, a side of $\Delta\Omega$ equals $2\pi\hbar/a$, i.e. is of the order of 6.6×10^{-27} g·cm·s^{-1}. Photons with such a difference in their

momentum vary only slightly in their wavelength, namely,

$$\Delta\lambda = \Delta\left(\frac{2\pi\hbar}{p}\right) = -\frac{(2\pi\hbar)^2}{p^2}\frac{\Delta p}{2\pi\hbar} = -\frac{\lambda^2}{a}$$

This corresponds to a relative wavelength difference of

$$\left|\frac{\Delta\lambda}{\lambda}\right| = \frac{\lambda}{a}$$

A very small value is obtained even for light waves of the infrared range ($\lambda \sim 1$ to 10 μm), namely, 10^{-4} to 10^{-5}. It must be noted that the two wavelengths chosen are not neighbours, so that the difference between adjacent wavelengths is many times smaller. Consequently, although actually the momenta and the photon wavelengths corresponding to them are discrete, from the macroscopic viewpoint they may be treated as virtually continuous quantities.

Now let us consider the matter of the number of states per volume element $d\Omega$ of momentum space. Although such an element is considered to be infinitely small from the viewpoint of our macroscopic notions, it is actually much larger than $\Delta\Omega$. The required number of states dG equals the number of the momentum vectors terminating in $d\Omega$ and is calculated approximately as the quotient obtained in dividing $d\Omega$ by $\Delta\Omega$:

$$dG = \frac{d\Omega}{\Delta\Omega} = \frac{d\Omega}{(2\pi\hbar)^3}V \qquad (7.21)$$

The accuracy of this result grows with an increasing difference between $d\Omega$ and $\Delta\Omega$. A somewhat different interpretation of expression (7.21) is possible. The quantity $d\gamma = d\Omega V$ is a volume element of μ-space. Expression (7.21) can be written as

$$dG = \frac{d\gamma}{(2\pi\hbar)^3} \qquad (7.22)$$

whence it follows that *the number of states per volume element of μ-space is determined by formula* (7.22).

It is not difficult to show that the above result is of a quite general nature. Consider, for example, the part dV of the total volume of a vessel and the previous volume $d\Omega$ of the momentum space. The phase space volume element

$$d\gamma = d\Omega \, dV$$

which differs from the preceding value, corresponds to them. How many states fall to $d\gamma$? The separated small part dV

of the space in the vessel should be treated as a new vessel with smaller wall dimensions. By (7.20), an elementary cell in it has another, larger size, namely,

$$\Delta\Omega = \frac{(2\pi\hbar)^3}{\mathrm{d}V}$$

The number of states is

$$\mathrm{d}G = \frac{\mathrm{d}\Omega}{\Delta\Omega} = \frac{\mathrm{d}\Omega\,\mathrm{d}V}{(2\pi\hbar)^3} = \frac{\mathrm{d}\gamma}{(2\pi\hbar)^3}$$

In the new volume element of phase space, the number of states is smaller than in the one considered previously because the volume $\mathrm{d}V$ is smaller than V. But in the total volume V, the number of small volumes $\mathrm{d}V$ is $V/\mathrm{d}V$, so that the total number of states remains the same.

7.6. Quantization for Particles

Consider particles in a potential well. In quantum mechanics, their behaviour in many respects is similar to what occurs for radiation. As we have already mentioned in Sec. 7.2, a de Broglie wave, i.e. a monochromatic wave, is associated with every free particle. In an infinitely deep potential well, standing waves appear, and an integral number of half-waves must fit in along the length of a side of the well. As for radiation, it is more convenient to replace the standing waves with running ones and consider, in order to retain the proper number of independent variables, that independent waves running in opposite directions are possible, but that an integral number of waves fits in along the length of a side of the well. In other words, relations (7.19) giving the possible values of the momentum components hold for particles as well as for waves. Formula (7.22) determining the number of states per volume element of µ-space also holds for particles.

The relation between the momentum and the energy of a particle, namely, $\varepsilon = p^2/(2m_0)$ is known from classical mechanics. Hence, the possible values of the energy are

$$\varepsilon = \frac{(2\pi\hbar)^2}{2m_0}\left[\left(\frac{m_x}{a}\right)^2 + \left(\frac{m_y}{b}\right)^2 + \left(\frac{m_z}{c}\right)^2\right] \qquad (7.23)$$

Q antum mechanics leads to a conclusion that is unexpected from the viewpoint of classical notions. It was estab-

lished that *real identical particles, like photons, obey the indistinguishability principle.* This circumstance reflects the wave properties of particles and has been confirmed by experiments.

All particles in nature are divided into two groups differing in principle from each other. They are classified according to the intrinsic angular momentum. Originally and, as was later established, in a too simplified way, this was considered to be the angular momentum in the rotation of a particle about its axis. It was found that for some particles the projection of the angular momentum onto an arbitrarily chosen axis can have only half-integral values of the constant $\hbar$, and for others, only an integral value. For example, for electrons, only two values of the intrinsic angular momentum or, as it is called, the **spin**, are possible: $+\hbar/2$ and $-\hbar/2$, and for photons, the values $+\hbar$ and $-\hbar$. Particles with a half-integral value of their spin are known as Fermi particles or **fermions**, and particles with an integral spin are known as Bose particles or **bosons**.

The following difference of principle exists between them. *Fermions observe the Pauli exclusion principle, according to which only a single particle can be in a state with definite values of the quantum numbers and spin.* For instance, not more than two electrons can be in a state with the values m_x, m_y, and m_z of the quantum numbers, i.e. in a state with a given momentum, and they must differ from each other in one having a spin of $+\hbar/2$ and the other of $-\hbar/2$. *Bosons do not obey the Pauli exclusion principle, and an unlimited number of bosons can be in each state.*

Chapter 8

GRAND CANONICAL DISTRIBUTION

8.1. The Canonical Distribution in Quantum Statistics

In classical statistics, the Gibbs distribution, or, as it is called, the **canonical** distribution, has the form

$$\mathrm{d}W = \exp\left(\frac{F-\mathscr{E}}{kT}\right)\mathrm{d}\Gamma$$

It gives the probability of a system being in one of the states described by a point in a volume element of phase space $d\Gamma$.

In quantum mechanics, a system may also be in different states with a different energy, but unlike classical mechanics, these states are **discrete**, that is, for example, there is a state with the energy $\mathscr{E}_1$ and a state with the energy $\mathscr{E}_2$, but there are no states with an energy between $\mathscr{E}_1$ and $\mathscr{E}_2$.

In the following, we shall have in view only systems of the type of an ideal gas, i.e. collections of particles, the forces of interaction between which may be disregarded. Such systems are sufficiently simple to allow the final results to be obtained in a simple form, while on the other hand, the model of an ideal gas is quite often a good approximation to real physical systems.

In an ideal gas, the above statement becomes especially evident. Let ε_1, ε_2, . . . stand for the energies of the states of individual particles and n_1, n_2, . . . for the occupation numbers of these states, i.e. for the number of particles in a given state. For the energy of the entire system, we can write

$$\mathscr{E}_\nu = n_1 \varepsilon_1 + n_2 \varepsilon_2 + \ldots$$

where $\mathscr{E}_\nu$ is the energy of the system in the state with the number ν, in which n_1 particles have the energy ε_1, n_2 have the energy ε_2, and so on. Hence, the states of the system as a whole can be numbered by indicating all the occupation numbers:

$$\nu = \{n_1,\ n_2,\ \ldots\}$$

and upon a transition from one state to another, the energy takes on values differing by an integral number of quantities ε_1, ε_2, etc.

The extension of the Gibbs distribution to quantum mechanics consists in the statement that the probability of the state ν having the energy $\mathscr{E}_\nu$ is

$$W_\nu = \exp\left(\frac{F^* - \mathscr{E}_\nu}{kT}\right) \tag{8.1}$$

Here F^* is the **free energy of the quantum system**. It is determined by the normalization condition, i.e. by the condition that the probability of finding the system in any of all the states is unity:

$$\sum_\nu W_\nu = 1 \tag{8.2}$$

Since it follows from (8.2) that

$$\sum_{\nu} \exp\left(\frac{F^* - \mathscr{E}_\nu}{kT}\right) = \exp\left(\frac{F^*}{kT}\right) \sum_{\nu} \exp\left(-\frac{\mathscr{E}_\nu}{kT}\right) = 1$$

by introducing the concept of the **statistical sum** or the **partition function**

$$Z^* = \sum_{\nu} \exp\left(-\frac{\mathscr{E}_\nu}{kT}\right) \qquad (8.3)$$

we can write

$$F^* = -kT \ln Z^* \qquad (8.4)$$

Hence, *if we know the energies $\mathscr{E}_\nu$ of all the possible states of a system, we can calculate the partition function by* (8.3) *and then find the free energy of the system by* (8.4).

Formulas (8.1) and (8.3) are similar to expressions (5.12) and (5.13), but there is also an appreciable difference between them. It is due to two reasons.

First, in classical mechanics, the states of a system form a continuous sequence, or, in the language of the probability theory, the state of a system is a continuous random variable (more exactly, the energy of a state is a continuous random variable), whereas in quantum mechanics the states are discrete.

Second, in the quantum-mechanical consideration, the indistinguishability principle must be taken into account, and also the Pauli exclusion principle for fermions.

Consequently, the quantum-mechanical free energy F^* does not coincide with the classical free energy F. On the one hand, this difference reflects the real distinction due to the fact that actually the laws of quantum mechanics are accurate, while the classical laws are an approximation of what actually occurs. This is justified far from always for systems of microparticles. On the other hand, there are systems for which it does not matter whether or not the indistinguishability and the Pauli exclusion principles are taken into account. Since in the majority of cases, the systems that are of practical interest consist of a very large number of microparticles so that the number of possible states is tremendous and the difference between close states is very small, they may be considered to be distributed continuously with a high degree of accuracy. It is clear that there must con-

sequently exist a relation between the quantum and the classical Gibbs distributions, and also between the free energies F^* and F. This relation will be established on a later page employing specific examples of bosons and fermions. Now we shall only consider a general procedure that is used for this purpose, and also an important corollary that follows from it.

Assume that the states of a system are discrete, and that the Pauli exclusion and indistinguishability principles may be disregarded. Each possible state of the system is represented by a point in phase gamma-space. For a discrete distribution, these points are at a certain distance from one another. Let g_Γ stand for the number of discrete states per unit volume of gamma-space, and let us call g_Γ the state density in gamma-space. The number of states per volume element $d\Gamma$ is

$$dG = g_\Gamma \, d\Gamma \qquad (8.5)$$

Assume that we have chosen such a small element $d\Gamma$ that the probability of all the states belonging to it is virtually the same. Since according to the Gibbs distribution, the probability depends on the energy, for this purpose it is sufficient that the energies of the states in $d\Gamma$ differ by a value much smaller than kT. Assume further that notwithstanding the smallness of the chosen volume $d\Gamma$, the number of possible discrete states falling to its share is sufficiently large. The partition function (8.3) can therefore be computed as follows.

We divide all the states depicted by points in gamma-space into groups belonging to the volumes $d\Gamma_i$ and perform summation in two stages: first over the states inside the individual volumes $d\Gamma_i$ $\left(\text{i.e.} \sum\limits_{d\Gamma_i} \right)$, and then add up the results obtained for the different volumes, i.e. we write

$$Z^* = \sum_i \left[\sum_{d\Gamma_i} \exp\left(-\frac{\mathscr{E}}{kT} \right) \right]$$

The sum in brackets is evaluated very simply. Indeed, according to our assumption, the value of the exponential for all the addends of this sum is the same, so that the value of the sum equals this quantity multiplied by the number of

terms in the sum, i.e. by the number of states in the volume $d\Gamma_i$, or with a view to (8.5)

$$\sum_{d\Gamma_i} \exp\left(-\frac{\mathscr{E}}{kT}\right) = \exp\left(-\frac{\mathscr{E}}{kT}\right) g_\Gamma \, d\Gamma$$

Hence,

$$Z^* = \sum_v \exp\left(-\frac{\mathscr{E}}{kT}\right) = \sum_i \exp\left(-\frac{\mathscr{E}}{kT}\right) g_\Gamma \, d\Gamma_i$$

Evaluation of the second sum over the different elements $d\Gamma_i$ is just integration over $d\Gamma$ so that

$$Z^* = \int \exp\left(-\frac{\mathscr{E}}{kT}\right) g_\Gamma \, d\Gamma \qquad (8.6)$$

Expression (8.6) can be seen to differ from the statistical integral (5.15)

$$Z = \int \exp\left(-\frac{\mathscr{E}}{kT}\right) d\Gamma$$

in the factor g_Γ. Since the latter is a constant quantity*, we have

$$Z^* = g_\Gamma Z \qquad (8.7)$$

For the free energy, we now obtain

$$F^* = -kT \ln Z^* = -kT \ln Z - kT \ln g_\Gamma$$
$$= F - kT \ln g_\Gamma \qquad (8.8)$$

Examination of formula (8.8) reveals that the free energy determined by (8.4) does not coincide with that determined classically by (5.14). Does this difference tell in determining experimentally observed quantities?

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* By (7.22), the number of states of one of the particles of a system in its mu-space is $d\gamma/(2\pi\hbar)^3$. The number of states of the system equals the product of the number of states of the individual particles, so that

$$g_\Gamma \, d\Gamma = \frac{d\gamma_1}{(2\pi\hbar)^3} \frac{d\gamma_2}{(2\pi\hbar)^3} \cdots \frac{d\gamma_N}{(2\pi\hbar)^3}$$

Since $d\Gamma = d\gamma_1 \, d\gamma_2 \ldots d\gamma_N$, we have

$$g_\Gamma = \left[\frac{1}{(2\pi\hbar)^3}\right]^N$$

We shall begin with the thermodynamic meaning of the free energy. A change in the free energy ΔF^* in an isothermal process, when the second term on the right-hand side of (8.8) is constant, equals the change ΔF, i.e. the work ΔA done by the system in an isothermal process, but taken with the opposite sign,

$$(\Delta F^*)_{T=\text{const}} = (\Delta F)_{T=\text{const}} = -\Delta A \qquad (8.9)$$

If we differentiate (8.8) with respect to the volume, we find

$$\frac{\partial F^*}{\partial V} = \frac{\partial F}{\partial V} = -P \qquad (8.10)$$

Hence, the equation of state is determined by the same equation.

For the internal energy, we obtain

$$U = F - T \frac{\partial F}{\partial T} = (F^* + kT \ln g_\Gamma) - T \left(\frac{\partial F^*}{\partial T} + k \ln g_\Gamma \right)$$

$$= F^* - T \frac{\partial F^*}{\partial T} \qquad (8.11)$$

i.e. the Gibbs-Helmholtz equation retains its form.

If by analogy with (6.17) we define the entropy by the relation

$$S^* = -\frac{\partial F^*}{\partial T} \qquad (8.12)$$

it is not difficult to show that this definition leads to a value of the entropy differing from what follows from expression (6.17) by a constant quantity. Indeed,

$$S^* = -\frac{\partial F^*}{\partial T} = -\frac{\partial F}{\partial T} + k \ln g_\Gamma = S + k \ln g_\Gamma$$

We must treat this difference in somewhat greater detail.

8.2. Entropy and the Third Law of Thermodynamics

In Sec. 6.4, we established the statistical meaning of the entropy. The final result obtained there has one appreciable shortcoming, and to understand this matter, we shall repeat the previous derivation, but as applied to the quantum Gibbs distribution.

It follows from the Gibbs-Helmholtz equation and the definition of the entropy S^* according to (8.12) that

$$S^* = \frac{U - F^*}{T}$$

But the internal energy is the mean value of the energy of a system, i.e.

$$U = \sum_{\nu} \mathscr{E}_{\nu} \exp\left(\frac{F^* - \mathscr{E}_{\nu}}{kT}\right)$$

therefore, using the normalization condition, we can write

$$S^* = \frac{1}{T} \sum_{\nu} \mathscr{E}_{\nu} \exp\left(\frac{F^* - \mathscr{E}_{\nu}}{kT}\right) - \frac{1}{T} \sum_{\nu} F^* \exp\left(\frac{F^* - \mathscr{E}_{\nu}}{kT}\right)$$

$$= -\sum_{\nu} \left(\frac{F^* - \mathscr{E}_{\nu}}{T}\right) \exp\left(\frac{F^* - \mathscr{E}_{\nu}}{kT}\right) \qquad (8.13)$$

Multiplying and dividing (8.13) by the Boltzmann constant k, we obtain

$$S^* = -k \sum_{\nu} \frac{F^* - \mathscr{E}_{\nu}}{kT} \exp\left(\frac{F^* - \mathscr{E}_{\nu}}{kT}\right) = -k \sum_{\nu} W_{\nu} \ln W_{\nu} \qquad (8.14)$$

i.e., *the entropy to within a constant quantity equals the mean value of the logarithm of the probability of the state in a system.* A glance at formula (8.14) shows that since the probability is a dimensionless quantity, the entropy coincides in dimension with the Boltzmann constant. Matters are somewhat different for formula (6.17)

$$S = -k \int \ln w \, d\Gamma$$

which differs in that it contains the probability density w instead of the probability W_{ν} and summation is replaced with integration. Since the probability density is a quantity having a dimension that is the reciprocal of the dimension of a phase volume element, the logarithm of the dimensional quantity is inside the integral, i.e. the dimension of the entropy is more complicated than in the preceding case. It is simple to see that the difference between (8.14) and (6.17) is obtained for the following reason.

The correct transition from the discrete quantum case to the classical continuous one must consist in replacing the probability W_v with the probability $w \, d\Gamma$ of the system being in one of the states belonging to $d\Gamma$. Hence, Eq. (5.14) yields

$$S^* = -k \sum w \, d\Gamma \ln (w \, d\Gamma) = -k \int \ln (w \, d\Gamma) \, w \, d\Gamma$$

$$= -k \int w \ln w \, d\Gamma - k \int \ln (d\Gamma) \, w \, d\Gamma$$

The quantity $d\Gamma$ is an infinitely small volume of phase space from a physical point of view. If we consider that all the elements $d\Gamma$ into which the phase space is divided are the same, when account is taken of the normalization condition, the last term becomes

$$-k \int \ln (d\Gamma) \, w \, d\Gamma = -k \ln (d\Gamma) \int w \, d\Gamma = -k \ln (d\Gamma)$$

Consequently, a strict transition from (8.14) to a continuous distribution leads to a formula differing from (6.17) by a constant quantity:

$$S^* = -k \int w \ln w \, d\Gamma - k \ln (d\Gamma) = -k \int w \ln w \, d\Gamma + \text{const}$$

The constant depends on the magnitude of the phase space volume element chosen as the infinitely small integration element, i.e. it is actually arbitrary. Hence, the entropy is determined classically only to within an arbitrary constant. This is no hindrance if, as is usual practice, one is interested in the difference of the entropy values in two states because the constant vanishes in subtraction. Formula (6.17), however, does not give the absolute value of the entropy.

Do experimental facts exist pointing to the advantages of one of the two expressions for the entropy? It seems they do. The behaviour of a number of thermodynamic quantities agrees with the assumption that cooling is attended by diminishing of the entropy and that its value at absolute zero is zero. Consequently, the arbitrary constant mentioned above must be chosen so as to satisfy the equation

$$S|_{T=0} = 0$$

This condition plays an important role in thermodynamics and was named its **third law**. It is not difficult to show that the third law is a result of determining the entropy by expression (8.14) taking into account the quantum discreteness of states if only we assume that the ground state of the system is not degenerate, i.e. there is only one ground state with the lowest value of the energy.

Indeed, assume that the state whose energy is the closest has an energy that is higher by $\Delta\mathscr{E}$. It therefore follows from the Gibbs distribution (8.1) that upon cooling to temperatures so low that $kT \ll \Delta\mathscr{E}$, the probability of all the states except the ground one will be negligibly small. At $T = 0$, the probability of the ground state is unity, and of all the other states is zero. In this case, the sum $\sum\limits_{\nu} W_{\nu} \ln W_{\nu}$ determining the entropy vanishes.

Consequently, taking of the quantum effects into account leads to a proper expression for the entropy having the form of (8.14), from which, particularly, for real systems we obtain the equality of the entropy to zero at $T = 0$, i.e. the third law of thermodynamics.

8.3. Maximum Entropy Principle

The entropy when properly determined by the quantum formula (8.14) coincides to within the factor k with (2.23) and, consequently, is a measure of the disorder or randomness of the macroscopic state of a system. An important principle whose correctness follows from the Gibbs distribution and is also established according to the coincidence of all the conclusions reached on its basis with experimental results is the maximum entropy principle. *The entropy is determined by formula* (8.14) *and in the equilibrium state reaches a maximum value compatible with the conditions in which a system is, in other words, an equilibrium state corresponds to the most disordered or random of all possible ones.* This principle can be taken as the cornerstone of the statistical physics of equilibrium states because, particularly, the Gibbs distribution follows from it.

Let us see at what value of the probabilities W_{ν} of individual states the entropy reaches its maximum value. For this purpose, we must use the rule for finding an extremum

and take into account that the probabilities W_ν are related by the normalization condition (8.2):

$$\sum_\nu W_\nu = 1 \qquad (8.15)$$

According to the general method of Lagrangian multipliers, we form the function

$$f(W_\nu) = -k \sum_\nu W_\nu \ln W_\nu - \lambda_1 \sum_\nu W_\nu$$

where λ_1 is a Lagrangian undetermined multiplier. Differentiation of $f(W_\nu)$ with respect to each of the variables W_ν and equating of the derivatives to zero yields a system of equations of which the ν-th one is

$$-k - k \ln W_\nu - \lambda_1 = 0$$

that is,

$$\ln W_\nu = -\left(1 + \frac{\lambda_1}{k}\right)$$

whence

$$W_\nu = \exp\left[-\left(1 + \frac{\lambda_1}{k}\right)\right] = \text{const}$$

where the value of the constant is determined from the normalization condition.

Hence, the probabilities of all the states are the same. Since the number of states of a system is infinitely large, from the normalization condition we obtain $W_\nu \to 0$. For the value of the entropy, with a view to all the W_ν's being equal, we have

$$S^* = -k \sum_\nu W_\nu \ln W_\nu = -k \ln W_\nu \sum_\nu W_\nu = -k \ln W_\nu$$

When W_ν tends to zero, $-\ln W_\nu$ tends to infinity so that the value of the entropy is infinite.

This result contradicts experimental facts and the Gibbs distribution according to which the probabilities of states with different energies are not the same. It was obtained because we did not take into account a very important circumstance. In real conditions, a system in equilibrium is not isolated, but is in contact with its surroundings. Customarily, the concept of a **heat bath** or **heat reservoir** is introduced to define a system interacting with the one under

consideration, but so large that the action of the system being studied cannot violate the equilibrium state of the heat bath. Since equilibrium is observed upon contact with the heat bath, the system being studied continuously exchanges energy with it. Consequently, although the energy is not constant, its mean value, i.e. the internal energy, has a strictly definite value. Hence, when finding the value of the probabilities W_ν, we must impose the following supplementary condition

$$\sum_\nu \mathscr{E}_\nu W_\nu = U = \text{const} \tag{8.16}$$

In finding the maximum, we now form the function

$$f_1(W_\nu) = -k \sum_\nu W_\nu \ln W_\nu - \lambda_1 \sum_\nu W_\nu - \lambda_2 \sum_\nu \mathscr{E}_\nu W_\nu$$

where λ_2 is a new Lagrangian undetermined multiplier. After differentiation, we obtain an equation of the kind

$$-k \ln W_\nu - k - \lambda_1 - \lambda_2 \mathscr{E}_\nu = 0$$

whence

$$W_\nu = \exp\left[-\left(1 + \frac{\lambda_1}{k} + \frac{\lambda_2}{k} \mathscr{E}_\nu \right) \right]$$

If we designate the multiplier λ_2 by $1/T$, and λ_1 by $-[(F^*/T) + k]$, the probability of the state ν is

$$W_\nu = \exp\left(\frac{F^* - \mathscr{E}_\nu}{kT} \right) \tag{8.17}$$

i.e., it coincides with the Gibbs distribution. The free energy introduced formally through the multiplier λ_1 and the temperature introduced through the multiplier λ_2 are determined by the normalization condition (8.15) and Eq. (8.16), substituting for W_ν its value from (8.17):

$$\sum_\nu \exp\left(\frac{F^* - \mathscr{E}_\nu}{kT} \right) = 1 \quad \text{and} \quad \sum_\nu \mathscr{E}_\nu \exp\left(\frac{F^* - \mathscr{E}_\nu}{kT} \right) = U \tag{8.18}$$

In establishing the relation between the free energy, the temperature, and the internal energy, it is more convenient to consider that the temperature is set, and not the internal energy. Equations (8.18) can be used to evaluate F^* and U as functions of T (and the volume V).

8.4. Derivation of the Grand Canonical Gibbs Distribution

By proceeding from the maximum entropy principle, we can obtain a more general distribution than the Gibbs one which we considered up to now. This is the case when the number of particles forming a system may vary. For instance, if a closed vessel contains a gas having a definite number of molecules, we can mentally separate a small volume and consider the gas in it as a system. Molecules can fly into the separated volume and fly out of it so that the exact number of molecules is not definite, but their mean number remains the same in equilibrium. We shall immediately take account of the quantum discreteness of the states because it can be seen from what has been said above that such an approach is more consistent.

Let $W_{\nu N}$ stand for the probability of occurrence of the νN-th state of a system consisting of N particles. Now the maximum of the entropy will correspond to a distribution such that gives the maximum of the expression

$$S^* = -k \sum_{\nu N} W_{\nu N} \ln W_{\nu N}$$

with the supplementary conditions

$$\sum_{\nu N} W_{\nu N} = 1, \quad \sum_{\nu N} \mathscr{E}_{\nu N} W_{\nu N} = U$$

$$\sum_{\nu N} N W_{\nu N} = \langle N \rangle$$

where $\langle N \rangle$ is the mean number of particles in the given system. We form the function

$$f_2(W_{\nu N}) = -k \sum_{\nu N} W_{\nu N} \ln W_{\nu N} - \lambda_1 \sum_{\nu N} W_{\nu N}$$

$$- \lambda_2 \sum_{\nu N} \mathscr{E}_{\nu N} W_{\nu N} - \lambda_3 \sum_{\nu N} N W_{\nu N}$$

Differentiation with respect to $W_{\nu N}$ yields the equation

$$- k \ln W_{\nu N} - k - \lambda_1 - \lambda_2 \mathscr{E}_{\nu N} - \lambda_3 N = 0$$

whose solution has the form

$$W_{\nu N} = \exp \left(-\frac{k + \lambda_1 + \lambda_2 \mathscr{E}_{\nu N} + \lambda_3 N}{k} \right)$$

or, introducing the notation

$$- (k + \lambda_1) = \frac{\Omega^*}{T}, \quad \lambda_2 = \frac{1}{T}, \quad \lambda_3 = -\frac{\mu}{T}$$

we have

$$W_{\nu N} = \exp\left(\frac{\Omega^* - \mathscr{E}_{\nu N} + \mu N}{kT}\right) \qquad (8.19)$$

Formula (8.19) *giving the probability of a system in equilibrium with a heat bath containing N particles and having the energy $\mathscr{E}_{\nu N}$ is known as the* **grand canonical Gibbs distribution.**

The quantities Ω^*, T, and μ we have introduced formally are determined from the conditions

$$\sum_{\nu N} W_{\nu N} = \sum_{\nu N} \exp\left(\frac{\Omega^* - \mathscr{E}_{\nu N} + \mu N}{kT}\right) = 1 \qquad (8.20)$$

$$\sum_{\nu N} W_{\nu N} \mathscr{E}_{\nu N} = \sum_{\nu N} \mathscr{E}_{\nu N} \exp\left(\frac{\Omega^* - \mathscr{E}_{\nu N} + \mu N}{kT}\right) = U \qquad (8.21)$$

$$\sum_{\nu N} W_{\nu N} N = \sum_{\nu N} N \exp\left(\frac{\Omega^* - \mathscr{E}_{\nu N} + \mu N}{kT}\right) = \langle N \rangle \qquad (8.22)$$

Instead of determining the values of μ and T corresponding to the given value of the internal energy U and the mean number of particles $\langle N \rangle$, we can consider them set, and then use Eqs. (8.20), (8.21), and (8.22) to find Ω^*, U, and $\langle N \rangle$ as functions of μ and T (and also of the system's volume V).

8.5. Thermodynamic Meaning of the Parameters Ω^*, μ, and T

In the method of deriving the grand canonical Gibbs distribution used above, the quantities Ω^*, μ, and the temperature T appeared as constants. Our next task is therefore the establishment of the physical meaning of these parameters. To do this, we can try with the aid of Eqs. (8.20), (8.21), and (8.22) to obtain equations relating these parameters, and compare the equations thus obtained with others known from thermodynamics, i.e. in the long run from experiments. This procedure presumes a good preliminary acquaintance with thermodynamics. It is therefore simpler, proceeding from an analogy with the ordinary Gibbs distribution, to acknowledge that T is the temperature, and

Ω^* is a function of T and μ similar to the free energy. We shall call it the **omega-potential**. Now, Eqs. (8.20)-(8.22) can be used to derive thermodynamic equations.

Following this programme, we shall begin with finding of the conditions in which two equilibrium systems are in equilibrium with each other. Assume that one system is described by the grand canonical distribution

$$W'_{\nu'N'} = \exp\left(\frac{\Omega^{*\prime} - \mathscr{E}'_{\nu'N'} + \mu'N'}{kT'}\right) \tag{8.23}$$

and the second by the distribution

$$W''_{\nu''N''} = \exp\left(\frac{\Omega^{*\prime\prime} - \mathscr{E}''_{\nu''N''} + \mu''N''}{kT''}\right) \tag{8.24}$$

Assume further that the energy of interaction of these systems with each other and with the heat bath is much smaller than that of the systems themselves. If we treat them as a single system, they obey a grand canonical distribution that can be written in the form

$$W_{\nu N} = \exp\left(\frac{\Omega^* - \mathscr{E}_{\nu N} + \mu N}{kT}\right) \tag{8.25}$$

Since we disregarded the interaction of the systems, the probability of any state of the first system does not depend on what the state of the second one is. In addition, each state of the combined system can be considered as a certain state of the first system and a certain independent state of the second one, so that each number (state index) νN corresponds to the numbers $\nu'N'$ and $\nu''N''$; here

$$N = N' + N'' \tag{8.26}$$

and

$$\mathscr{E}_{\nu N} = \mathscr{E}'_{\nu'N'} + \mathscr{E}''_{\nu''N''} \tag{8.27}$$

i.e. the total number of particles equals the sum of the particles in each of the constituent systems, and the total energy equals the sum of the energies.

If the states of the subsystems are independent, in accordance with the fundamentals of the probability theory, the probability of the state of a compound system equals the product of the probabilities of the states in the subsystems forming it:

$$W_{\nu N} = W'_{\nu'N'} W''_{\nu''N''} \tag{8.28}$$

Substituting for the probabilites in (8.28) their values from (8.23), (8.24), and (8.25), we obtain

$$\exp\left(\frac{\Omega^* - \mathscr{E}_{\nu N} + \mu N}{kT}\right) = \exp\left(\frac{\Omega^{*\prime} - \mathscr{E}_{\nu' N'}' + \mu' N'}{kT'}\right)$$
$$= \exp\left(\frac{\Omega^{*\prime\prime} - \mathscr{E}_{\nu'' N''}'' + \mu'' N''}{kT''}\right)$$

or, using (8.26) and (8.25), we have

$$\exp\left(\frac{\Omega^* - \mathscr{E}_{\nu' N'}' - \mathscr{E}_{\nu'' N''}'' + \mu N' + \mu N''}{kT}\right)$$
$$= \exp\left(\frac{\Omega^{*\prime} - \mathscr{E}_{\nu' N'}' + \mu' N'}{kT'}\right) \exp\left(\frac{\Omega'' - \mathscr{E}_{\nu'' N''}'' + \mu'' N''}{kT''}\right) \quad (8.29)$$

Since Eq. (8.29) must be identical for all the values $\mathscr{E}_{\nu' N'}'$, $\mathscr{E}_{\nu'' N''}''$, N', N'', this signifies that the following equalities must be observed:

$$T = T' = T'' \tag{8.30}$$

$$\mu = \mu' = \mu'' \tag{8.31}$$

$$\Omega^* = \Omega^{*\prime} + \Omega^{*\prime\prime} \tag{8.32}$$

Hence, *for the equilibrium of two systems, it is necessary that their temperatures T and parameters μ (called the chemical potentials) be equal. In addition, the omega-potential of the compound system equals the sum of the omega-potentials of the constituent systems.*

It can be seen from the above that the chemical potential plays the same role with respect to the number of particles as the temperature does with respect to the energy. Since in all systems that are in equilibrium with a given heat bath, the temperatures and chemical potentials have the same value as the value of these quantities for the heat bath, they may be considered to be characteristics of the heat bath, and not of the individual systems in equilibrium with it. For exactly this reason, it is good practice to consider μ and T to be set, and determine the other quantities describing the given system (its omega-potential, internal energy, etc.) as functions of these parameters.

Quite a few important thermodynamic relations can be obtained from the normalization condition. For example, after differentiation of (8.20) with respect to the chemical

potential μ, we obtain

$$\sum_{\nu N} \frac{1}{kT} \left(\frac{\partial \Omega^*}{\partial \mu} + N \right) \exp \left(\frac{\Omega^* - \mathcal{E}_{\nu N} + \mu N}{kT} \right) = 0$$

or, if we use (8.21),

$$\frac{\partial \Omega^*}{\partial \mu} = - \langle N \rangle \qquad (8.33)$$

Consequently, the derivative of the omega-potential with respect to the chemical potential taken with the opposite sign equals the mean number of particles in the system.

Differentiation of the normalization condition with respect to the temperature leads to an equation similar to the Gibbs-Helmholtz equation for a system with a constant number of particles. We have

$$0 = \frac{\partial}{\partial T} \sum_{\nu N} \exp \left(\frac{\Omega^* - \mathcal{E}_{\nu N} + \mu N}{kT} \right)$$

$$= \sum_{\nu N} \frac{1}{kT} \frac{\partial \Omega^*}{\partial T} \exp \left(\frac{\Omega^* - \mathcal{E}_{\nu N} + \mu N}{kT} \right)$$

$$- \sum_{\nu N} \frac{\Omega^* - \mathcal{E}_{\nu N} + \mu N}{kT^2} \exp \left(\frac{\Omega^* - \mathcal{E}_{\nu N} + \mu N}{kT} \right) \qquad (8.34)$$

We can write (8.34) in the form

$$\frac{1}{kT} \frac{\partial \Omega^*}{\partial T} \sum_{\nu N} \exp \left(\frac{\Omega^* - \mathcal{E}_{\nu N} + \mu N}{kT} \right)$$

$$- \frac{\Omega^*}{kT^2} \sum_{\nu N} \exp \left(\frac{\Omega^* - \mathcal{E}_{\nu N} + \mu N}{kT} \right)$$

$$+ \frac{1}{kT^2} \sum_{\nu N} \mathcal{E}_{\nu N} \exp \left(\frac{\Omega^* - \mathcal{E}_{\nu N} + \mu N}{kT} \right)$$

$$- \frac{\mu}{kT^2} \sum_{\nu N} N \exp \left(\frac{\Omega^* - \mathcal{E}_{\nu N} + \mu N}{kT} \right) = 0 \qquad (8.35)$$

If we multiply Eq. (8.35) by kT^2 and use relations (8.20)-(8.22), we have

$$T \frac{\partial \Omega^*}{\partial T} - \Omega^* + U - \mu \langle N \rangle = 0$$

that is

$$U = \Omega^* - T\,\frac{\partial \Omega^*}{\partial T} + \mu\,\langle N \rangle$$

or finally

$$U = \Omega^* - T\,\frac{\partial \Omega^*}{\partial T} - \mu\,\frac{\partial \Omega^*}{\partial \mu} \qquad (8.36)$$

Expression (8.36) allows us to evaluate the internal energy according to the omega-potential and is a generalization of the Gibbs-Helmholtz equation for systems with a variable number of particles.

Differentiation of the normalization condition with respect to the volume V yields

$$0 = \frac{\partial \Omega^*}{\partial V} - \sum_{\nu N} \frac{\partial \mathscr{E}_{\nu N}}{\partial V}\,\exp\left(\frac{\Omega^* - \mathscr{E}_{\nu N} + \mu N}{kT}\right) \qquad (8.37)$$

Here account is taken of the circumstance that upon a change in the volume of the subsystem in equilibrium with the heat bath, the temperature and the chemical potential, which are determined by the heat bath, remain constant, whereas the energy of the system changes because of interaction with the walls. To form a more specific notion of the case being considered, we shall assume that the subsystem is a gas confined in a cylinder with a movable piston. The side wall of the cylinder has an opening through which the gas communicates with another larger vessel filled with the same gas (the heat bath). When the piston moves over a distance of dx, the volume of the subsystem (the gas in the cylinder) changes by dV, where

$$dV = S\,dx$$

(S is the area of the piston). For the volume derivative of the energy, we can write

$$\frac{\partial \mathscr{E}_{\nu N}}{\partial V} = \frac{1}{S}\,\frac{\partial \mathscr{E}_{\nu N}}{\partial x}$$

We bear in mind that the energy change $d\mathscr{E}_{\nu N}$ upon displacement of the piston by dx occurs with a constant number of particles N. The change in the energy equals the work of the force compressing the system, which was in the state νN, therefore,

$$dA = d\mathscr{E}_{\nu N} = F'_{\nu N}\,dx$$

According to Newton's third law, the system acts on the piston with an equal but oppositely directed force

$$F_{\nu N} = -F'_{\nu N} = -\frac{\partial \mathscr{E}_{\nu N}}{\partial x}$$

It thus follows from (8.37) that

$$\frac{\partial \Omega^*}{\partial V} = -\frac{1}{S} \sum_{\nu N} F_{\nu N} \exp\left(\frac{\Omega^* - \mathscr{E}_{\nu N} + \mu N}{kT}\right) = -\frac{\langle F \rangle}{S}$$

where $\langle F \rangle$ is the mean value of the force for all possible states. The mean force divided by the area is the pressure P exerted by the system on the piston, so that

$$P = -\frac{\partial \Omega^*}{\partial V} \tag{8.38}$$

Hence, *the pressure equals the volume derivative of the omega-potential taken with the opposite sign.*

Let us establish, finally, the relation between the omega-potential and the entropy. It follows from the general expression for the entropy with account taken of the grand canonical distribution that

$$S^* = -k \sum_{\nu N} W_{\nu N} \ln W_{\nu N}$$

$$= -k \sum_{\nu N} \frac{\Omega^* - \mathscr{E}_{\nu N} + \mu N}{kT} \exp\left(\frac{\Omega^* - \mathscr{E}_{\nu N} + \mu N}{kT}\right)$$

If we use the conditions (8.20)-(8.22), we find that

$$S^* = -\frac{1}{T}(\Omega^* - U + \mu \langle N \rangle) \tag{8.39}$$

With the help of the generalized Gibbs-Helmholtz equation, we can write (8.39) in the following form:

$$S^* = -\frac{1}{T}\left(\frac{\partial \Omega^*}{\partial T} T\right) = -\frac{\partial \Omega^*}{\partial T} \tag{8.40}$$

i.e. *the entropy equals the temperature derivative of the omega-potential taken with the opposite sign.*

Let us see what the change in the internal energy is for a reversible process in which the volume V, temperature T, and chemical potential μ experience an infinitely small change. From (8.36), we have

$$dU = d\Omega^* - dT \frac{\partial \Omega^*}{\partial T} - Td\left(\frac{\partial \Omega^*}{\partial T}\right) - d\mu \frac{\partial \Omega^*}{\partial \mu} - \mu d\left(\frac{\partial \Omega^*}{\partial \mu}\right)$$

This equation can be written as

$$dU = \frac{\partial \Omega^*}{\partial V} dV + \frac{\partial \Omega^*}{\partial T} dT + \frac{\partial \Omega^*}{\partial \mu} d\mu - dT \frac{\partial \Omega^*}{\partial T}$$

$$- Td\left(\frac{\partial \Omega^*}{\partial T}\right) - d\mu\left(\frac{\partial \Omega^*}{\partial \mu}\right) - \mu d\left(\frac{\partial \Omega^*}{\partial \mu}\right)$$

Upon collecting like terms and using relations (8.33), (8.38), and (8.40), we obtain

$$dU = -P\, dV + T\, dS^* + \mu d\langle N \rangle$$

When the number of particles in a system does not change $(d\langle N \rangle = 0)$, and no work is done $(dV = 0)$, the internal energy changes only at the expense of the supply of heat dQ; consequently,

$$dQ = T\, dS^*$$

For the change in the internal energy, we therefore find

$$dU = -dA + dQ + \mu d\langle N \rangle \qquad (8.41)$$

Hence, in a system with a varying number of particles, the internal energy changes not only owing to heat transfer and the performance of work, but also owing to a change in the mean number of particles. If the volume of a system does not change $(\Delta V = \Delta A = 0)$ and the system is adiabatically isolated $(\Delta S^* = \Delta Q = 0)$ it can be seen from (8.41) that $\mu = \Delta U / \Delta \langle N \rangle$, i.e. *the chemical potential is the change in the internal energy associated with the addition of the particle to a process in which ΔV and ΔS^* are zero.*

The omega-potential is a function of the volume of a system, and also of the temperature and chemical potential. When the mean number of particles is given instead of the chemical potential, it is more convenient to deal with another thermodynamic function determined by the equation

$$F^* = \Omega^* + \mu \langle N \rangle \qquad (8.42)$$

When the conditions (volume, temperature, mean number of particles) change, the function F^* experiences a change equal to

$$dF^* = d\Omega^* + \mu d\langle N \rangle + \langle N \rangle d\mu$$

Since

$$d\Omega^* = \frac{\partial \Omega^*}{\partial T} dT + \frac{\partial \Omega^*}{\partial V} dV + \frac{\partial \Omega^*}{\partial \mu} d\mu$$

$$= -S^*\, dT - P\, dV - \langle N \rangle d\mu$$

where relations (8.38), (8.33), and (8.40) have been taken into account, we have

$$dF^* = - S^* \, dT - P \, dV + \mu \, d\langle N \rangle \qquad (8.43)$$

With a constant mean number of particles and temperature, the change in the function we have introduced is

$$dF^* = - P \, dV$$

i.e., it equals the work with the opposite sign. This gives us the grounds, by analogy with the definition presented in Sec. 6.2, to call the function F^* the free energy. A glance at (8.43) shows that its use is convenient when the volume, temperature, and mean number of particles are taken as the independent variables. Systems with a preset number of particles may be treated as ones with a preset mean number of particles, therefore (8.42) is a direct generalization of the free energy considered earlier.

If the temperature and volume of a system do not change, while the mean number of particles increases by dN, by (8.43) the free energy receives the increment

$$dF^* = \mu d \langle N \rangle \qquad (8.44)$$

Examination of (8.44) reveals that

$$\mu = \frac{\partial F^*}{\partial N} \qquad (8.45)$$

i.e. *that from the thermodynamical viewpoint, the chemical potential is the change in the free energy of a system associated with the addition of one particle to it provided that the volume and temperature remain constant.*

It can be seen from (8.43) that at constant $\langle N \rangle$ and V, we have

$$\frac{\partial F^*}{\partial T} = - S^* \qquad (8.46)$$

and at constant $\langle N \rangle$ and T

$$\frac{\partial F^*}{\partial V} = - P \qquad (8.47)$$

These relations are similar to (6.12) and (6.17).

Exercise

1. *Proceeding from the expression for the omega-potential of an ideal monatomic classical gas*

$$\Omega^* = -(kT)^{5/2} \exp\left(\frac{\mu}{kT}\right) VC$$

where

$$C = 2\left(\frac{m}{2\pi\hbar^2}\right)^{3/2}$$

find the main thermodynamic characteristics of this system (the derivation of the formula for the omega-potential is given in Chap. 10).

Solution. (a) We find the mean number of particles by (8.33):

$$\langle N\rangle = -\frac{\partial\Omega^*}{\partial\mu} = (kT)^{3/2} \exp\left(\frac{\mu}{kT}\right) VC$$

Hence, particularly,

$$\mu = kT \ln\left[\frac{n}{C\,(kT)^{3/2}}\right] \tag{a}$$

where $n = \langle N\rangle/V$ is the concentration of the particles.

(b) The equation of state is found according to (8.38):

$$P = -\frac{\partial\Omega^*}{\partial V} = (kT)^{5/2} \exp\left(\frac{\mu}{kT}\right) C$$

If we eliminate μ with the help of Eq. (a), we obtain

$$P = nkT$$

(c) We compute the internal energy according to (8.36):

$$U = \Omega^* - T\,\frac{\partial\Omega^*}{\partial T} - \mu\,\frac{\partial\Omega^*}{\partial\mu} = \Omega^* - \frac{5}{2}\,\Omega^* + \frac{\mu}{kT}\,\Omega^* - \frac{\mu}{kT}\,\Omega^* = -\frac{3}{2}\,\Omega^*$$

or, if we use the expression for the mean number of particles, we have

$$U = \frac{3}{2}\,\langle N\rangle\,kT$$

(d) By (8.39), we obtain for the entropy

$$S^* = -\frac{1}{T}\left(\Omega^* + \frac{3}{2}\,\Omega^* + \frac{\mu}{kT}\,\Omega^*\right) = -\frac{1}{T}\left(\frac{5}{2} + \frac{\mu}{kT}\right)\Omega^*$$

If we take into consideration the relation between Ω^* and $\langle N\rangle$, and also Eq. (a) for μ, we find

$$S^* = -k\,\langle N\rangle\left[\frac{5}{2} + \ln\frac{n}{C\,(kT)^{3/2}}\right] \tag{b}$$

Equation (b) can be rewritten as

$$S^* = k\,\langle N\rangle\left[\ln V + \frac{3}{2}\ln T + C_1\right]$$

where

$$C_1 = \ln C + \frac{3}{2} \ln k - \frac{5}{2} - \ln \langle N \rangle$$

for which it was sufficient to use the definition of the concentration $n = \langle N \rangle / V$.

It will be useful to compare the final expression for the entropy with the one we obtained on a previous page for a fixed number of particles (see Sec. 6.4). The two expressions can be seen to differ only by a constant quantity.

Chapter 9

BOSE-EINSTEIN STATISTICS

9.1. Bosons

As already mentioned in Chap. 7, *bosons are defined to be particles with a zero or integral* (in units of $\hbar$) *spin.* They include:

(1) mesons (K and π) whose spin is zero;

(2) some atoms in which the spin of the electrons, protons, and neutrons forming them is summated so that the resultant spin is integral (an example is He_2);

(3) photons (spin is 1);

(4) phonons (sound wave quanta, spin is 1).

We shall be interested chiefly in photons because mesons are very short-lived particles (their lifetime is 10^{-8} s) whose role in the processes we are dealing with is usually insignificant; atoms, on the other hand, have such a large mass that most frequently classical statistics may be applied to them. At very low temperatures, however, the quantum effects must be taken into account.

For a substance in the solid state where the atoms form a crystal lattice, our task consists in studying the vibrations of the lattice or, in other words, in studying the properties of sound waves or sound quanta—phonons.

In the present chapter, a collection of bosons is treated as an ideal gas, i.e. it is assumed that interaction between the particles is absent.

9.2. Bose-Einstein Distribution

Consider an ideal boson gas from the statistical viewpoint. Virtually all information on its macroscopic properties is contained, as we have seen, in the omega-potential Ω^*, and therefore the evaluation of this function is our main task. As we have mentioned in the preceding chapter, it is convenient to assume that the system being considered is in equilibrium with a heat bath whose temperature T and chemical potential μ are set. Hence, to determine Ω^*, we must use the normalization condition (8.20) that can be written as

$$\sum_{\nu N} \exp\left(\frac{\Omega^* - \mathscr{E}_{\nu N} + \mu N}{kT}\right)$$

$$= \exp\left(\frac{\Omega^*}{kT}\right) \sum_{\nu N} \exp\left(\frac{-\mathscr{E}_{\nu N} + \mu N}{kT}\right) = \exp\left(\frac{\Omega^*}{kT}\right) Z^* = 1$$

where the partition function

$$Z^* = \sum_{\nu N} \exp\left(\frac{-\mathscr{E}_{\nu N} + \mu N}{kT}\right) \tag{9.1}$$

so that

$$\Omega^* = -kT \ln Z^* \tag{9.2}$$

Calculations are considerably facilitated if we choose the system in a special way, namely, if we consider as a system the particles of the boson gas that are in a definite state (have preset momentum components). Having determined the omega-potential of the earmarked particles (subsystem), we can then find the omega-potential of the entire gas as the sum of the expressions evaluated for all possible states. The use of such a method implies the employment of the grand canonical distribution because the number of particles in a given state is not fixed. A separated subsystem is one with a varying number of particles.

We shall thus consider particles in a definite state i, and let the energy of this state be $\mathscr{E}_i$. The energy of the subsystem depends on how many particles are in the state being considered, and if their number is n_i, we have

$$\mathscr{E}_{\nu N} = n_i \varepsilon_i \tag{9.3}$$

One state of the subsystem differs from another one only in the number of particles n_i so that for numbering the states of the subsystem, we can use this number. The partition function for the separated subsystem is

$$Z_i^* = \sum_{n_i} \exp\left(\frac{-\varepsilon_i n_i + \mu n_i}{kT}\right) \tag{9.4}$$

where summation is performed from $n_i = 0$, when there are no particles in the given state, to $n_i = \infty$. There may be any number of bosons in the selected subsystem since they do not obey the Pauli exclusion principle.

It is a simple matter to calculate the partition function because it can be seen to reduce to a geometrical progression

$$Z_i^* = \sum_{n_i=0}^{\infty} \left[\exp\left(\frac{-\varepsilon_i + \mu}{kT}\right)\right]^{n_i} = \frac{1}{1 - \exp\left[(-\varepsilon_i + \mu)/(kT)\right]}$$

Hence, for Ω_i^* (the index i shows that this expression relates to the i-th subsystem, i.e. to particles in the state i), we obtain

$$\Omega_i^* = kT \ln\left[1 - \exp\left(\frac{\mu - \varepsilon_i}{kT}\right)\right] \tag{9.5}$$

The omega-potential of the entire system of bosons can be written as

$$\Omega^* = \sum_i \Omega_i^* = kT \sum_i \ln\left[1 - \exp\left(\frac{\mu - \varepsilon_i}{kT}\right)\right] \tag{9.6}$$

where summation is performed over all possible states of the bosons, i.e. over all values of i.

We must note that in evaluating the partition function (9.4), we used the principle of particle indistinguishability. Indeed, we assumed that there is only one state whose energy is $n_i \varepsilon_i$. According to classical notions, when the particles are considered to be distinguishable, there may be very many such states. If the total number of particles in a system (a subsystem with a heat bath) is N, we can choose n_i particles from among N of them in ways so that the sets of n_i particles would differ from one another in at least the number of one particle

$$\frac{N!}{n_i!\,(N - n_i)!}$$

Hence, in evaluating the partition function in this case, we must write

$$Z_i = \sum_{n_i} \frac{N!}{n_i!\,(N-n_i)!} \exp\left(\frac{-n_i \varepsilon_i + \mu' n_i}{kT}\right)$$

where account is taken of the fact that the values of the chemical potential μ' of the classical system and of the partition function Z_i may differ from those of μ and Z_i^*. Since it is assumed when using the grand canonical distribution that any number of particles may enter the subsystem being considered, then N must be infinitely large, and to calculate Z_i we must perform a limiting process when $N \to \infty$. If we take into account that when $N \gg n_i$, we have

$$\frac{N!}{n_i!\,(N-n_i)!} = \frac{N\,(N-1)\,\ldots\,(N-n_i+1)}{n_i!} \approx \frac{N^{n_i}}{n_i!}$$

then

$$Z_i = \sum_{n_i} \frac{N^{n_i}}{n_i!} \exp\left(\frac{-\varepsilon_i + \mu'}{kT}\,n_i\right)$$

$$= \sum_{n_i} \frac{1}{n_i!} \left[\exp\left(\frac{-\varepsilon_i + \mu' + kT \ln N}{kT}\right)\right]^{n_i}$$

Since N is infinitely large, the above sum can have a meaning only if the chemical potential μ' is also infinite so that when added to the term $kT \ln N$ it yields a finite expression. It is therefore expedient to deal with the finite quantity μ equal to

$$\mu = \mu' + kT \ln N$$

and call it the chemical potential of the system. Hence,

$$Z_i = \sum_{n_i} \frac{1}{n_i!} \left[\exp\left(\frac{-\varepsilon_i + \mu}{kT}\right)\right]^{n_i}$$

This expression is a Maclaurin expansion of the exponential function so that

$$Z_i = \exp\left[\exp\left(\frac{-\varepsilon_i + \mu}{kT}\right)\right]$$

For the omega-potential of the i-th subsystem, we find

$$\Omega_i = -kT \exp\left(\frac{-\varepsilon_i + \mu}{kT}\right) \tag{9.7}$$

and for the omega-potential of the entire system

$$\Omega = \sum_i \Omega_i = -kT \sum_i \exp\left(\frac{-\varepsilon_i + \mu}{kT}\right) \qquad (9.8)$$

Expressions (9.5) and (9.7) are different, but if in (9.5) the chemical potential is much smaller than ε_i so that

$$\varepsilon_i - \mu \gg kT$$

the exponent in the exponential is a large negative number:

$$\frac{\mu - \varepsilon_i}{kT} \ll -1$$

In this case, the exponential itself is very small, and we approximately have

$$\ln\left[1 - \exp\left(\frac{\mu - \varepsilon_i}{kT}\right)\right] \approx -\exp\left(\frac{\mu - \varepsilon_i}{kT}\right) \qquad (9.9)$$

Consequently, *the omega-potential of a boson gas differs from that of classical particles because of the indistinguishability principle, but at very small (large negative) values of the chemical potential this difference becomes insignificant.* For the omega-potential of the entire boson gas to coincide with the classical value, the chemical potential μ must be at least several kT's smaller than the lowest level of the system's energy because now the approximation (9.9) holds for all states of the bosons.

When the omega-potential is known, it is not difficult to find the most diverse characteristics of a system.

Let us find, for example, the mean number of bosons in a given state. By (8.33) and (9.5), we have

$$\langle n_i \rangle = -\frac{\partial \Omega_i^*}{\partial \mu} = \frac{\exp\left[(\mu - \varepsilon_i)/(kT)\right]}{1 - \exp\left[(\mu - \varepsilon_i)/(kT)\right]}$$

or

$$\langle n_i \rangle = \frac{1}{\exp\left[(\varepsilon_i - \mu)/(kT)\right] - 1} \qquad (9.10)$$

Formula (9.10) determining the mean number of bosons in a state with the energy ε_i is known as the **Bose-Einstein distribution,**

For the internal energy of the system of all the bosons, we find by (8.36) and (9.6) that

$$U = \sum_i \frac{\varepsilon_i}{\exp\left[(\varepsilon_i - \mu)/(kT)\right] - 1} = \sum_i \varepsilon_i \langle n_i \rangle$$

This is the natural result if we take into account that ε_i is the energy of the bosons, and $\langle n_i \rangle$ is their mean number in the state *i*.

We can calculate other thermodynamic quantities characterizing a boson gas in a similar way. These quantities are often expressed in terms of the mean values of the occupation numbers, and this is just what determines the great importance of the Bose-Einstein distribution.

9.3. Photons

Let us now apply the results obtained above to a photon gas, i.e. to electromagnetic radiation.

A photon gas has an important feature distinguishing it from bosons having a finite rest mass. This feature is associated with the fact that the number of bosons in a photon gas is not limited. For example, by heating the walls of a vessel (heat bath), we can increase the density of the electromagnetic radiation inside the vessel unlimitedly, i.e. increase the number of photons contained in it.

In deriving the grand canonical distribution from the maximum entropy principle (see Sec. 8.4), we used the condition

$$\sum_{\nu N} N W_{\nu N} = \langle N \rangle$$

in which the mean number of particles in the system $\langle N \rangle$ was considered to be set. This condition is superfluous for photons because their mean number is determined by the temperature and volume of the system. If it is not imposed (which can be taken into account formally by assuming the multiplier $\lambda_3 = -\mu/T$ to be zero, i.e. actually considering that $\mu = 0$), we arrive at the conclusion that *the grand canonical distribution can be used for photons at a value of the chemical potential equal to zero.*

By formula (9.10), the mean number of bosons at the i-th evel is

$$\langle n_i \rangle = \frac{1}{\exp\left[(\hbar\omega_i - \mu)/(kT)\right] - 1}$$

For photons, the Bose-Einstein distribution has the form

$$\langle n_i \rangle = \frac{1}{\exp\left[\hbar\omega_i/(kT)\right] - 1} \tag{9.11}$$

Another important feature of a photon gas, as, incidentally, of an ideal gas of any bosons, is that although the possible energy levels of the system are discrete, in the majority of practically interesting cases they are arranged so close that they may be considered almost continuous. Let us stop in greater detail on this feature.

To evaluate the omega-potential, we must find the sum

$$\Omega^* = kT \sum_i \ln\left[1 - \exp\left(\frac{\mu - \varepsilon_i}{kT}\right)\right]$$

If the energy levels ε_i are so close to one another that the difference between neighbours is much smaller than kT, the sum written above may be replaced, with a negligible approximation, by an integral over the energy. Indeed, let $d\varepsilon$ be a small interval of energies that, on the one hand, is much smaller than kT, and on the other is much larger than the interval between adjacent energy levels, so that $d\varepsilon$ contains many energy levels. It is convenient to perform summation in two steps. We divide the entire energy scale into intervals having the size $d\varepsilon$ and first summate the addends relating to one interval. Since within the limits of one interval $d\varepsilon$ the energies differ from one another by an amount that is much smaller than kT, all the addends have approximately the same value, and their sum equals one of them multiplied by the number of levels in the interval $d\varepsilon$.

We shall designate the number of levels in $d\varepsilon$, which for small energy intervals is proportional to the magnitude of the interval, by $g_\varepsilon\, d\varepsilon$, where g_ε is a function named the **density of states** and having the meaning of the number of levels per unit interval of energy in the vicinity of the energy $d\varepsilon$. For instance, for the omega-potential, the required sum

will have the form

$$kT \ln \left[1 - \exp \left(\frac{\mu - \varepsilon}{kT} \right) \right] g_\varepsilon \, d\varepsilon$$

It remains for us to perform summation over the various intervals $d\varepsilon$, which, as can readily be seen, reduces to integration. We thus obtain the following expression for the omega-potential:

$$\Omega^* = kT \int\limits_0^\infty \ln \left[1 - \exp \left(\frac{\mu - \varepsilon}{kT} \right) \right] g_\varepsilon \, d\varepsilon \qquad (9.12)$$

Summation is performed from the lowest, zero level of the energy to an infinitely large one.

For actual evaluation of the integral (9.12), we must know the density of states $g_\varepsilon \, d\varepsilon$, and we shall now pass over to its calculation.

Almost all the necessary calculations were performed earlier. Indeed, the following relation holds between the energy ε and the momentum p of a photon:

$$\varepsilon = pc$$

where c is the speed of light, so that the energy interval from ε to $\varepsilon + d\varepsilon$ will contain all states whose momentum magnitude is larger than $p = \varepsilon/c$ and smaller than

$$p + dp = \frac{\varepsilon}{c} + \frac{d\varepsilon}{c}$$

In other words, the states that in the momentum space are depicted by points in a spherical layer of thickness dp belong to the energy interval $d\varepsilon$. Since the volume of such a layer is $d\Omega = 4\pi p^2 \, dp$, the number of states in it, by formula (7.21), is

$$dG = \frac{4\pi p^2 \, dp}{(2\pi\hbar)^3} V \qquad (9.13)$$

If we express the momentum in terms of the energy, we obtain

$$dG = \frac{4\pi\varepsilon^2 \, d\varepsilon}{(2\pi\hbar c)^3} V \qquad (9.14)$$

where dG is the number of states in the energy interval $d\varepsilon$. According to the definition of the density of states intro-

duced above, we have

$$dG = g_\varepsilon \, d\varepsilon$$

so that from (9.14) we obtain an explicit expression for this function:

$$g_\varepsilon \, d\varepsilon = \frac{4\pi\varepsilon^2}{(2\pi\hbar c)^3} V \, d\varepsilon \qquad (9.15)$$

When applying (9.15) to a photon gas, we must bear in mind that there are two kinds of electromagnetic waves and, therefore, of photons differing from each other in their polarization. Formula (9.13) holds for each kind. Consequently, if we are interested in the entire photon gas, and not in one of its components having a given polarization, we must multiply (9.15) by the number of components, i.e. by two.

With a view to the last remark, we obtain the following formula for the omega-potential of a photon gas whose chemical potential is zero:

$$\Omega^* = 2kT \int_0^\infty \ln \left[1 - \exp \left(-\frac{\varepsilon}{kT} \right) \right] \frac{4\pi\varepsilon^2}{(2\pi\hbar c)^3} \, d\varepsilon V \qquad (9.16)$$

Expression (9.16) is often used in a form when the frequency ω, related to the energy by the expression $\varepsilon = \hbar\omega$, is chosen as the integration variable. In this representation, we have

$$\Omega^* = 2kT \int_0^\infty \ln \left[1 - \exp \left(-\frac{\hbar\omega}{kT} \right) \right] \frac{4\pi\omega^2}{(2\pi c)^3} \, d\omega V \qquad (9.17)$$

The quantity

$$d\Omega^* = 2kTV \ln \left[1 - \exp \left(-\frac{\hbar\omega}{kT} \right) \right] \frac{4\pi\omega^2}{(2\pi c)^3} \, d\omega \qquad (9.18)$$

has the meaning of the omega-potential of all photons whose frequency is within the interval $d\omega$, and therefore the function

$$S_{\Omega^*}(\omega) = 2kTV \frac{4\pi\omega^2}{(2\pi c)^3} \ln \left[1 - \exp \left(-\frac{\hbar\omega}{kT} \right) \right] \qquad (9.19)$$

can be called the **spectral density** of the omega-potential.

To calculate (9.17), it is convenient to introduce a new integration variable

$$x = \frac{\hbar\omega}{kT}$$

The formula for Ω^* therefore becomes

$$\Omega^* = \frac{(kT)^4}{\pi^2 \hbar^3 c^3} V \int_0^\infty \ln\left(1 - e^{-x}\right) x^2 \, dx$$

Since*

$$\int_0^\infty \ln\left(1 - e^{-x}\right) x^2 \, dx \approx -2.15$$

then

$$\Omega^* = -2.15 \frac{k^4}{\pi^2 \hbar^3 c^3} V T^4 \tag{9.20}$$

Hence, *when the energy levels may be considered continuous, the omega-potential of a photon gas is determined by expression (9.20) or in the spectral form by Eq. (9.18).*

Let us now see when the approximation of the continuous distribution of energy levels holds. It is obvious that this happens only with sufficiently high temperatures because the main criterion is the smallness of the distance between the levels in comparison with kT. The condition of quasicontinuity will be satisfied if the energy kT is larger than the energy of the lowest state, since the states of a system include those corresponding to one, two, etc. photons being on the lowest level, with all other levels vacant. In other words, the intervals between adjacent levels are certainly smaller than $\hbar\omega_0$, where ω_0 is the lowest frequency of the oscillations possible in the system.

Assume, for example, that we have a cubic container with a side of $a = 1$ cm. The lowest frequency is determined from the condition that the wavelength corresponding to it is a. Strictly speaking, oscillations are possible in a metal container when half a wavelength is accommodated within its

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$$\int_0^\infty \ln\left(1 - e^{-x}\right) x^2 \, dx = -\int_0^\infty \sum_{k=1}^\infty \frac{e^{-kx}}{k} x^2 \, dx$$

$$= -\sum_{k=1}^\infty \frac{1}{k^4} \int_0^\infty e^{-y} y^2 \, dy = -2 \sum_{k=1}^\infty \frac{1}{k^4} \approx -2 \cdot \frac{\pi^4}{90} \approx -2.15$$

(see [19], p. 297).

side, so that for the lowest frequency the replacement of standing waves with running ones according to the rule set out in Sec. 7.3 is a rather poor approximation. But since we are interested in observance of the condition

$$\hbar\omega_0 \ll kT \tag{9.21}$$

with a large margin, the difference in the factor of the order of two is of no significance. Consequently, in the example being considered, the maximum wavelength is of the order of $a = 1$ cm, and the lowest frequency is thus

$$v_0 = \frac{c}{\lambda} = \frac{c}{a}$$

i.e. $v_0 \approx 3 \times 10^{10}$ Hz. The intervals between energy levels are smaller than $2\pi\hbar v_0 = 2 \times 10^{-23}$ J, and the condition (9.21) is satisfied already at temperatures of the order of 10 K, when $kT = 1.38 \times 10^{-22}$ J. If the container is cooled to a temperature of the order of 0.1 K, the transition from formula (9.6), taking into account the discrete structure of the levels, to formula (9.12), where they are assumed to be continuous, is illegitimate.

9.4. Laws of Thermal Radiation

A knowledge of the omega-potential allows us to calculate many important characteristics of a photon gas in equilibrium, i.e. of equilibrium thermal radiation. One of the most interesting parameters is the internal energy U. Using formula (8.36) and applying it to (9.18), we shall find the following expression for the internal energy of photons whose frequency is within the interval $d\omega$ provided that $\mu = 0$:

$$dU = d\Omega^* - T\frac{\partial}{\partial T}(d\Omega^*) = \frac{8\pi\omega^2\,d\omega}{(2\pi c)^3}\,V\,\frac{1}{\exp\left[\hbar\omega/(kT)\right] - 1}\,\hbar\omega \tag{9.22}$$

Expression (9.22) can be interpreted as follows. The first factor is the number of states per frequency interval $d\omega$. The second factor determines the mean number of photons in a state with the frequency ω so that its product by the first factor gives the mean number of photons in the frequency

interval from ω to $\omega + d\omega$:

$$dN = \frac{8\pi\omega^2\, d\omega}{(2\pi c)^3} \frac{V}{\exp\left[\hbar\omega/(kT)\right] - 1} \qquad (9.23)$$

The last factor is the energy of one photon, and therefore multiplication of (9.23) by $\hbar\omega$ leads to an expression for the mean energy of a photon gas within the frequency interval being considered.

If a small opening that does not virtually violate the equilibrium state of the photon gas is made in a cavity containing thermal radiation, a certain amount of the radiation emerges from the opening. The power of this radiation within the frequency interval $d\omega = 1$ related to a unit of area is called the **spectral density of the radiant emittance** (we shall call it the **emissivity** for brevity's sake) and is designated in the following by r_ω. It is a simple matter to calculate this quantity, using the results of Sec. 3.9. Indeed, there we obtained expression (3.53) for the density of a particle flux, namely,

$$j = \frac{n v_{\mathrm{m}}}{4}$$

If by dj we understand the density of a flux of photons having a frequency within the interval $d\omega$, their concentration $n\,(\omega)\,d\omega$, as follows from formula (9.23), is

$$n\,(\omega)\ d\omega = \frac{dN}{V} = \frac{8\pi\omega^2\, d\omega}{(2\pi c)^3\,\{\exp\left[\hbar\omega/(kT)\right] - 1\}} \qquad (9.24)$$

Since the velocity of all the photons is the same and equals c, we have

$$dj = \frac{8\pi\omega^2\, d\omega}{(2\pi c)^3} \frac{1}{\exp\left[\hbar\omega/(kT)\right] - 1} \frac{c}{4} \qquad (9.25)$$

Each photon carries along with it the energy $\hbar\omega$, therefore (9.25) helps us obtain the following expression for the emissivity, which by definition relates to a unit interval of frequencies $d\omega$:

$$r_\omega\, d\omega = \hbar\omega\, dj = \frac{\hbar\omega^3\, d\omega}{(2\pi c)^2\,\{\exp\left[\hbar\omega/(kT)\right] - 1\}} \qquad (9.26)$$

If radiation is incident on the opening considered above from outside, it completely passes into the cavity without experiencing reflection. When the cavity is large enough,

we may also disregard the emerging radiation due to reflection from the internal walls. Hence, a cavity with an opening is what is known as a **blackbody**, i.e. a body completely absorbing all the radiation incident on it. Consequently, *formula* (9.26) *determines the emissivity of a blackbody*. It was named the **Planck formula** after the scientist who first derived it. Figure 9.1 shows plots of the Planck function against the frequency for several temperatures.
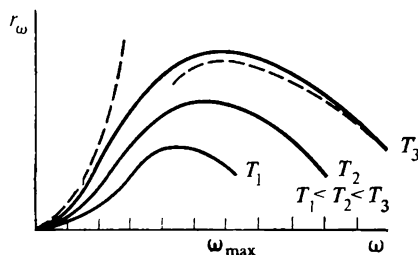
Fig. 9.1

For low frequencies, when $\hbar\omega/kT \ll 1$, the exponential in the denominator of (9.26) may be expanded into a series, and only the first two terms taken:

$$\exp\left(\frac{\hbar\omega}{kT}\right) \approx 1 + \frac{\hbar\omega}{kT} \tag{9.27}$$

Substitution of this expansion into (9.26) yields

$$r_\omega \, d\omega \approx \frac{\omega^2}{(2\pi c)^2} kT \, d\omega \tag{9.28}$$

The approximate formula (9.28) is known as the **Rayleigh-Jeans formula** and shows that in the region of low frequencies, the emissivity of a blackbody is proportional to the square of the frequency. Historically, this relation was obtained earlier than the Planck formula from purely classical considerations, and according to the classical theory ought to be obeyed for all frequencies. The total radiation energy according to this formula equals infinity:

$$\int_0^\infty r_\omega \, d\omega = \frac{kT}{(2\pi c)^2} \int_0^\infty \omega^2 \, d\omega$$

because the last integral diverges. Hence, the classical theory was not able to explain radiation because it led to an absurd result. Relation (9.28) is depicted in Fig.9.1 by the dashed line in the region of low frequencies.

At high frequencies, when $\hbar\omega/kT \gg 1$, the exponential in the denominator of (9.26) is much larger than unity. If the latter is disregarded, we obtain what is known as **Wien's formula**:

$$r_\omega \, d\omega \approx \frac{\hbar\omega^3}{(2\pi c)^2} \exp\left(-\frac{\hbar\omega}{kT}\right) d\omega \tag{9.29}$$

examination of which shows that at high frequencies the emissivity rapidly (exponentially) shrinks to zero. Wien's law is shown in Fig. 9.1 by the dashed line in the region of high frequencies.

The position of the peak on an emissivity curve can be determined if we differentiate r_ω with respect to ω and equate the derivative to zero. We have

$$\frac{dr_\omega}{d\omega} = \frac{d}{d\omega}\left\{\frac{\hbar\omega^3}{(2\pi c)^2}\frac{1}{\exp\left[\hbar\omega/(kT)\right]-1}\right\}$$

$$=\frac{\hbar}{(2\pi c)^2}\left\{\frac{3\omega^2}{\exp\left[\hbar\omega/(kT)\right]-1} - \frac{\omega^3\left[\hbar/(kT)\right]\exp\left[\hbar\omega/(kT)\right]}{\{\exp\left[\hbar\omega/(kT)\right]-1\}^2}\right\}=0$$

This equation is reduced to the form

$$3\left[\exp\left(\frac{\hbar\omega}{kT}\right)-1\right]-\frac{\hbar\omega}{kT}\exp\left(\frac{\hbar\omega}{kT}\right)=0$$

or

$$\frac{\hbar\omega}{kT}=3-3\exp\left(-\frac{\hbar\omega}{kT}\right)$$

From the last relation by consecutive approximations it is a simple matter to obtain

$$\left(\frac{\hbar\omega}{kT}\right)_0 = 3$$

$$\left(\frac{\hbar\omega}{kT}\right)_1 = 3 - e^{-3}\times 3 = 2.85$$

$$\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot$$

$$\frac{\hbar\omega}{kT}=2.82$$

Hence, the peak of the emissivity corresponds to the frequency

$$\omega_{max}=2.82\,\frac{k}{\hbar}\,T \tag{9.30}$$

which is directly proportional to the absolute temperature. This relation is called the **Wien displacement law** and shows that *for higher temperatures the peak is displaced in the direction of shorter wavelengths (higher frequencies)*.

The total power emitted by a blackbody from a unit of surface area is known as the **radiant emittance**. It can be determined by calculating the integral

$$R_e = \int_0^\infty r_\omega \, d\omega = \int_0^\infty \frac{\hbar \omega^3 \, d\omega}{(2\pi c)^2 \{ \exp [\hbar \omega / (kT)] - 1 \}}$$

If we introduce the new integration variable $x = \hbar \omega / (kT)$, we have*

$$R_e = \frac{(kT)^4}{(2\pi c)^2 \hbar^3} \int_0^\infty \frac{x^3 \, dx}{e^x - 1} = \sigma T^4 \qquad (9.31)$$

where

$$\sigma = 6.49 \frac{k^4}{(2\pi c)^2 \hbar^3} = 5.67 \times 10^{-8} \, \text{W m}^{-2} \text{K}^{-4} \qquad (9.32)$$

Relation (9.31) is known as the **Stefan-Boltzmann law** and shows that *the radiant emittance is proportional to the fourth power of the absolute temperature*. The constant σ is called the **Stefan-Boltzmann constant**.

We shall show in concluding how the use of mathematical techniques makes it possible to compute the pressure exerted by thermal radiation on the walls of a cavity. By formula (8.38) with a view to (9.20), we find

$$P = -\frac{\partial \Omega^*}{\partial V} = -\frac{\partial}{\partial V} \left(-2.15 \frac{k^4}{\pi^2 \hbar^3 c^3} V T^4 \right) = \frac{4}{3} \frac{\sigma}{c} T^4$$

Hence, thermal radiation exerts on the walls of the cavity confining it a pressure that is proportional to the fourth power of the temperature. It is interesting to note that the pressure does not depend on the volume. This reflects the

---

*
$$\int_0^\infty \frac{x^3 \, dx}{e^x - 1} = \int_0^\infty \frac{x^3 e^{-x}}{1 - e^{-x}} \, dx = \int_0^\infty \sum_{m=1}^\infty x^3 e^{-mx} \, dx$$

$$= \sum_{m=1}^\infty \int_0^\infty x^3 e^{-mx} \, dx = \sum_{m=1}^\infty \frac{3!}{m^4} = 6 \sum_{m=1}^\infty \frac{3!}{m^4} = 6 \times \frac{\pi^4}{90} \approx 6.49$$

(see [19], p. 297)

circumstance that the number of photons in the cavity is not fixed. An increase in the volume is attended by the appearance of new photons so that their concentration, which depends only on the temperature, is conserved.

9.5. Phonons

Boson statistics can also be used for describing phenomena relating to an absolutely different field.

At low temperatures, when quantum effects become especially significant, most substances are in the solid state, and their atoms form crystal lattices. The displacement of an atom in a lattice calls forth the displacement of neighbouring atoms and thus leads to the appearance of a wave propagating along the crystal. *The wave nature of the motion of atoms in a crystal lattice makes it possible to build up a statistical theory of crystals by analogy with the theory of thermal radiation in a cavity.* The comprehensive theory is considerably more intricate than for electromagnetic waves because a lattice is discrete and vibrations of various kinds are possible in it (in the simplest cases they are divided into longitudinal and transverse vibrations). Finally, the properties of a crystal and, consequently, of the waves may vary in different directions (anisotropy). To simplify our treatment, we can, as is often done, approximately replace a real lattice with a continuous isotropic medium having the same elastic parameters as the lattice does. Actually, this consists in the assumption that the crystal lattice may be replaced with an elastic medium in which the velocity of propagation of sound waves (compression, dilatation, and displacement waves) is the same as in the lattice and is identical in all directions. Altogether three possible kinds of vibrations are considered, of which two correspond to transverse waves with two mutually perpendicular directions of polarization and one to a longitudinal wave. Theory gives the same result for each kind of vibrations, and the difference is only that the speed of sound for longitudinal and transverse waves is different. Bearing this in mind, we shall limit our treatment to only a longitudinal wave whose speed of propagation will be designated by c_l.

If a crystal has limited dimensions, for example the shape of a parallelepiped with the sides a, b, and c, then vibrations

of strictly definite frequencies are possible in it. The vibration frequencies depend on the dimensions of the crystal and the conditions of reflection at its free boundaries. Although, strictly speaking, the set of possible frequencies is discrete, it may be considered continuous in almost all practically interesting cases. In this approximation, the exact value of each individual frequency is not so important. It is much more significant to determine the distribution density of these frequencies, i.e. the number dG of various waves whose frequencies are within the interval $d\omega$. In other words, it is necessary to find the density of states g_ω, where

$$dG = g_\omega d\omega$$

By complete analogy with electromagnetic waves, it is convenient to assume that only those frequencies are possible for which the components of the wave vector **k**, where

$$|\mathbf{k}| = k = \frac{2\pi}{\lambda} = \frac{\omega}{c_1}$$

(c_1 is the speed of sound replacing the speed of propagation of electromagnetic waves c) are determined by relations of the form of (7.16):

$$k_x = \frac{2\pi}{a} m_x, \quad k_y = \frac{2\pi}{b} m_y, \quad k_z = \frac{2\pi}{c} m_z \qquad (9.33)$$

where m_x, m_y, and m_z are integers.

There is, however, an important distinction from light waves that is associated with the discrete structure of the crystal lattice. The spectrum of frequencies of electromagnetic waves is not limited from above, so that unlimitedly high frequencies or unlimitedly small wavelengths are possible. In crystals, waves with a wavelength smaller than the value λ_{min} cannot exist. This property issues from the discreteness of the lattice, and it can be explained with the greatest clarity using Fig. 9.2, which depicts transverse waves with a diminishing wavelength for a one-dimensional train of atoms (designated by dots). The last of them corresponds to the smallest possible value of the wavelength, equal to the doubled lattice constant when neighbouring atoms vibrate in counterphase.

The theory of thermal vibrations of a lattice can thus be reduced to the theory of equilibrium sound waves similar

to the theory of equilibrium electromagnetic radiation and differing from the latter in that the possible types of waves are limited by the minimum wavelength λ_{min} or by the maximum frequency

$$\omega_{max} = \frac{2\pi c_l}{\lambda_{min}} \qquad (9.34)$$

corresponding to it.

For internal agreement of the theory, the value of ω_{max} must be chosen proceeding from the condition that the total number of different waves in a crystal equals the number
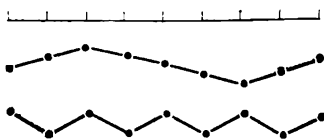
Fig. 9.2

of degrees of freedom of its constituent atoms. If the number of atoms is N, and since each atom has three degrees of freedom, the total number of degrees of freedom is $3N$. This signifies that in a simple lattice there are N different wavelengths for each of the kinds of vibrations (longitudinal and two transverse). The condition determining ω_{max} can thus be written as

$$\int_0^{\omega_{max}} \frac{4\pi\omega^2 \, d\omega}{(2\pi c_l)^3} \, V = N$$

that is

$$\frac{4\pi}{3} \frac{\omega_{max}^3}{(2\pi c_l)^3} \, V = N \quad \text{or} \quad \omega_{max} = \sqrt[3]{6\pi^2} \left(\frac{N}{V}\right)^{1/3} c_l$$

In a simple cubic crystal, the volume of one atom is d^3, where d is the constant of the cubic lattice. We can therefore write the last expression in the form

$$\omega_{max} = \frac{\sqrt[3]{6\pi^2} \, c_l}{d} = \frac{2\pi c_l}{1.61d} \qquad (9.35)$$

from which it follows, particularly, that $\lambda_{min} = 1.61d$.

Using the condition of the limitedness of sound wave frequencies, we can write by analogy with (9.17) for the omega-

potential

$$\Omega^* = \int\limits_0^{\omega_{max}} kT \ln\left[1 - \exp\left(-\frac{\hbar\omega}{kT} \right) \right] \frac{4\pi\omega^2\,d\omega}{(2\pi c_1)^3} V \quad (9.36)$$

Formula (9.36) relates to waves of one type, for instance longitudinal ones, and for this reason the factor 2 present in (9.17) and taking into account the two possible polarizations of electromagnetic waves has been dropped in it.

Two cases must be distinguished.

If the upper integration limit is much larger than $kT/\hbar$, upon integration we shall also have to do with the frequencies ω for which $\omega \gg kT/\hbar$, i.e.

$$\exp\left(-\frac{\hbar\omega}{kT} \right) \ll 1$$

Since for these frequencies

$$\ln\left[1 - \exp\left(-\frac{\hbar\omega}{kT} \right) \right] \approx \exp\left(-\frac{\hbar\omega}{kT} \right)$$

is a very small quantity, the upper integration limit can be extended to infinity without an appreciable error, and now the theory completely coincides with that of electromagnetic radiation. Instead of photons, we speak of **phonons** (sound quanta); the role of the speed of light is played by that of sound, and all the laws obtained for thermal radiation hold for phonons.

Particularly, by analogy with (9.20), for each type of waves (longitudinal and two transverse types), we have

$$\Omega^* = -1.07 \frac{k^4}{\pi^2\hbar^3 c_{ph}^3} VT^4 \quad (9.37)$$

where c_{ph} is the speed of the corresponding wave. We can next find various thermodynamic characteristics of a crystal lattice in the conventional way. For instance, using the Gibbs-Helmholtz equation, we obtain an expression for the internal energy associated with each wave type

$$U = \Omega^* - T\frac{\partial\Omega^*}{\partial T} = -3\Omega^* = 3.21\frac{k^4}{\pi^2\hbar^3 c_{ph}^3} VT^4$$

Here account is taken of the fact that for phonons $\mu = 0$.

The heat capacity at constant volume of a crystal is the sum of three similar terms each of which is due to one type

of vibrations and equals

$$c_V = \frac{\partial U}{\partial T} = 12.84 \frac{k^4}{\pi^2 \hbar^3 c_{ph}^3} V T^3 \qquad (9.38)$$

When the temperature lowers, the heat capacity rapidly (like T^3) tends to zero.

In the other limiting case, ω_{max} is much smaller than $kT/\hbar$. All the frequencies that are taken into account in the integral are such in this case that

$$\frac{\hbar\omega}{kT} \ll 1$$

Consequently, for instance, for the internal energy of the phonons of longitudinal vibrations whose frequencies are within the interval $d\omega$, in accordance with (9.22), by expanding the exponential into a series and limiting ourselves to the first two terms, we can obtain

$$dU = \frac{4\pi\omega^2 \, d\omega}{(2\pi c_{ph})^3} V \frac{\hbar\omega}{\exp[\hbar\omega/(kT)] - 1} \approx \frac{4\pi\omega^2 \, d\omega}{(2\pi c_{ph})^3} VkT \qquad (9.39)$$

Equation (9.39) corresponds to the theorem of the uniform distribution of the energy among the degrees of freedom that holds in the classical case. The first factor determines the number of states within the frequency interval $d\omega$, and the second one shows that to each state there falls the mean energy kT (of which $kT/2$ falls to the kinetic and $kT/2$ to the potential energy in the wave). If for electromagnetic oscillations, the formula corresponding to the classical approximation led to an absurd result (to an infinitely large total internal energy), for sound waves this is not obtained because there is an upper limit of the possible frequencies for them. The internal energy in this limiting case is described by the expression

$$U = \int_0^{\omega_{max}} \frac{4\pi\omega^2 \, d\omega}{(2\pi c_1)^3} VkT = \frac{4}{3} \pi\omega_{max}^3 \frac{V}{(2\pi c_1)^3} kT \qquad (9.40)$$

If we take into account the value of ω_{max} by formula (9.35), the formula for the internal energy of longitudinal waves can be written as

$$U = NkT \qquad (9.41)$$

Since two types of transverse vibrations are possible in a crystal in addition to the longitudinal vibrations, the total internal energy in the limiting case being considered is

$$U = 3NkT \qquad (9.42)$$

This is in complete agreement with the Boltzmann principle. Indeed, an atom of a lattice has three degrees of freedom (motion along the axes x, y, and z), the energy kT falling to each degree of freedom ($kT/2$ to the kinetic and $kT/2$ to the potential energy). The total mean energy of one atom is $3kT$ and, consequently, the internal energy of a lattice is equal to that given by (9.42).

In this case, we obtain a constant value for the heat capacity:

$$C_V = \frac{\partial U}{\partial T} = 3Nk$$

The two limiting cases considered above correspond to low and high temperatures. The criterion of their observance can be written as follows: when

$$T \ll \frac{\hbar \omega_{max}}{k} = \frac{\hbar}{k} \sqrt[3]{6\pi^2} \, \frac{c_{ph}}{d} = \Theta_D$$

quantum formulas hold, and when

$$T \gg \frac{\hbar \omega_{max}}{k} = \frac{\hbar}{k} \sqrt[3]{6\pi^2} \, \frac{c_{ph}}{d} = \Theta_D$$

classical ones (the principle of uniform distribution of energy among the degrees of freedom). The parameter Θ_D depending on the universal constants ($\hbar$, k) and the lattice parameters for a given specific crystal (c_{ph}, d) has the dimension of temperature and is known as the **Debye temperature** for this crystal. Hence, if the temperature at which a crystal is exceeds the Debye temperature significantly, classical statistics may be used, whereas if it is of the same order or lower, quantum statistics come to the forefront. The quantum formulas are considerably simplified, becoming analogues of the formulas for thermal radiation, at a temperature much lower than the Debye temperature. It must be borne in mind that the Debye temperatures differ for longitudinal and transverse waves because the speeds of propagation of these waves are different.

Exercises

1. *If the area of a radar aerial is* $S = 10$ m², *and its receiving device registers signals in the frequency band width of* 1 mHz *at a wavelength of* 0.03 m, *what will the power of the noise signal be when the aerial is directed towards the Sun? The Sun's temperature is* $T_S = 6000$ K, *the square of the ratio between the Sun's radius and the radius of the Earth's orbit is* $\xi = 2.17 \times 10^{-5}$.

Solution. The Sun's radiation corresponds to thermal radiation at a temperature of 6000 K. For a wavelength of $\lambda = 3$ cm, the ratio $\hbar\omega/kT_S$ is

$$\frac{\hbar\omega}{kT_S} = \frac{2\pi\hbar c}{k\lambda T_S} \approx 10^{-4} \ll 1$$

so that for the emissivity we can use formula (9.28), where in the given case $d\omega = 2\pi \times 10^6$ s^{-1}. With an increase in the distance from the Sun, the energy density diminishes inversely proportional to the square of the distance, so that a unit of the Earth's area receives the power

$$\xi\varepsilon(\omega)\,d\omega = \xi\,\frac{\omega^2 kT_S}{(2\pi c)^2}\,d\omega$$

The total power received by an aerial of area S is

$$S\xi\varepsilon(\omega)\,d\omega = S\xi\,\frac{\omega^2}{(2\pi c)^2}\,kT_S\,d\omega$$

Introducing numerical values, we find the magnitude of the noise signal: 2×10^{-14} W.

2. *Assess the molar heat capacity of copper at a temperature of* 900 *and* -200 °C *(the speed of longitudinal waves in copper is* 4700 m/s, *of transverse waves is* 2260 m/s, *the density of copper is* 8.9 g/cm³, *the atomic mass is* 64 g/mol; *assume that the lattice constant equals* 0.228 nm).

Solution. For the Debye temperature of longitudinal waves, we find $\Theta_D = \sqrt[3]{6\pi^2}\hbar c_{ph}/(kd) = 618$ K, and for transverse waves, $\Theta_D = 297$ K. For a temperature of 900 °C, the heat capacity may be evaluated by formula (9.42), which yields 25 J/(K mol) for the molar heat capacity. For a temperature of -200 °C (or 73 K), we use the formula

$$C_{\mu V} = 12.84\,\frac{k^4}{\pi^2\hbar^3 c_{ph}^3}\,VT^3$$

whence for longitudinal waves we obtain 1.16 J/(K mol), and for each type of transverse wave 10 J/(K mol) (we determine the volume V from the ratio of the atomic mass to the density).

Chapter 10

FERMI-DIRAC STATISTICS

10.1. Fermions

Particles having a half-integral spin (in units of $\hbar$) are called fermions. Unlike bosons, in addition to the indistinguishability principle, they obey the Pauli exclusion principle. This imposes special restrictions on the distribution of fermions among the possible states, so that the statistics of fermions or, as is also said, the Fermi-Dirac statistics differs very considerably from the Bose-Einstein statistics treated in the preceding chapter.

Fermions include:
(1) electrons,
(2) positrons,
(3) nucleons (protons and neutrons), and
(4) certain nuclei and atoms.

Electrons are of the greatest interest because positrons are encountered rarely in natural conditions (they rapidly annihilate with electrons), while the masses of nucleons, nuclei, and atoms are so large that classical statistics may be applied to them in the majority of cases.

We have already mentioned above that at very low temperatures, when the quantum effects become especially significant, a substance is usually in the solid crystalline state, and it is therefore convenient to consider its statistical properties by introducing the notion of phonons (see Sec. 9.5). Phonons are bosons regardless of whether the crystal lattice is built up of bosons or of fermions.

10.2. Fermi-Dirac Distribution

Let us consider an ideal gas of electrons, i.e. we shall assume that the interaction of the electrons with one another may be disregarded. At first sight, such an assumption seems to be unsubstantiated because electrons have a charge, and the electrical forces which they interact with are quite appreciable. We can, however, take the interaction of the electrons into account approximately by the method of the self-consistent field (see Sec. 4.6), i.e. assume that they are in an

external electric field equivalent to the field set up by the electrons themselves. In the particular case of a gas-discharge plasma or electrons in a solid body (metals, semiconductors), the equivalent field often vanishes or is very small because the negative charge of the electrons is compensated by the charge of the positive ions equal to it on an average.

A system of non-interacting electrons can be characterized by indicating the collection of the possible states of the individual electrons and by their distribution among these states. As was done for an ideal gas of bosons, let us choose as a subsystem a single state having the number i. If the energy of this state is ε_i, then according to the grand canonical distribution (the subsystem is constantly exchanging electrons with the remaining part of the system taken as a heat bath), we obtain the following expression for the omega-potential of the subsystem:

$$\Omega_i^* = -kT \ln Z_i^* = -kT \sum_n \exp\left(\frac{n\mu - \varepsilon_i n}{kT}\right) \qquad (10.1)$$

Formally, the partition function in (10.1) is similar to the function (9.4) that was written for a boson gas. An appreciable distinction appears, however, owing to account being taken of the Pauli exclusion principle. If for bosons, summation over the number of particles in a given state was performed from $n = 0$ to $n = \infty$, for fermions, according to the Pauli principle, n may have only two values: $n = 0$, and $n = 1$. Hence,

$$Z_i^* = \sum_n \exp\left(\frac{n\mu - n\varepsilon_i}{kT}\right) = 1 + \exp\left(\frac{\mu - \varepsilon_i}{kT}\right)$$

and

$$\Omega_i^* = -kT \ln\left[1 + \exp\left(\frac{\mu - \varepsilon}{kT}\right)\right] \qquad (10.2)$$

Formula (10.2) differs from the corresponding formula (9.5) holding for bosons in the sign before the exponential.

The omega-potential of the entire system is obtained by summation of the omega-potentials of all the subsystems, i.e. by summation over all possible states:

$$\Omega^* = \sum_i \Omega_i^* = -kT \sum_i \ln\left[1 + \exp\left(\frac{\mu - \varepsilon_i}{kT}\right)\right] \qquad (10.3)$$

The entire thermodynamics of an ideal electron gas follows from relations (10.2) *and* (10.3). Let us find, particularly, an expression for the mean number of particles in the state i. By the general rule (8.33), we have

$$\langle n_i \rangle = -\frac{\partial \Omega_i^*}{\partial \mu} = \frac{\exp\left[(\mu - \varepsilon_i)/(kT)\right]}{1 + \exp\left[(\mu - \varepsilon_i)/(kT)\right]} = \frac{1}{\exp\left[(\varepsilon_i - \mu)/(kT)\right] + 1} \tag{10.4}$$

Formula (10.4) determining the mean number of particles in a state having the energy ε_i is known as the **Fermi-Dirac distribution.**

The chemical potential μ can be found from the condition that the total mean number of particles in a system equals the sum of the mean numbers in the individual states:

$$\langle N \rangle = \sum_i \langle n_i \rangle = \sum_i \frac{1}{\exp\left[(\mu - \varepsilon_i)/(kT)\right] + 1} \tag{10.5}$$

Formula (10.5) also follows directly from (10.3) if we write

$$\langle N \rangle = -\frac{\partial \Omega^*}{\partial \mu} = -\frac{\partial}{\partial \mu} \sum_i \Omega_i^*$$

$$= \sum_i \frac{1}{\exp\left[(\mu - \varepsilon_i)/(kT)\right] + 1}$$

For the internal energy, we have according to (8.36)

$$U = \Omega^* - T\frac{\partial \Omega^*}{\partial T} + \mu\frac{\partial \Omega^*}{\partial \mu} = -kT \sum_i \ln\left[1 + \exp\left(\frac{\mu - \varepsilon_i}{kT}\right)\right]$$

$$- T\left[-k\sum_i \ln\left[1 + \exp\left(\frac{\mu - \varepsilon_i}{kT}\right)\right]\right]$$

$$- kT \sum_i \frac{\exp\left[(\mu - \varepsilon_i)/(kT)\right]}{\{1 + \exp\left[(\mu - \varepsilon_i)/(kT)\right]\}}\left(\frac{\mu - \varepsilon_i}{kT^2}\right)\right] + \mu N \tag{10.6}$$

where the condition (10.5) has been used. After collecting like terms, we obtain from (10.6):

$$U = \sum_i \frac{\varepsilon_i}{\exp\left[(\varepsilon_i - \mu)/(kT)\right] + 1} \tag{10.7}$$

The important formula (10.7) determines the internal energy of an ideal gas of fermions and has the meaning of the pro-

ducts of the energies of particles and their mean number in each of the possible states, i.e.

$$U = \sum_i \varepsilon_i \langle n_i \rangle \qquad (10.8)$$

10.3. Electron Gas in a Potential Well

An electron gas in a potential well is an important example in a practical respect because in a definite approximation metals and semiconductors can be treated in this way. Since the state of an electron in a potential well is set according to (7.19) by the components of its momentum, and the energy is related to the momentum by the formula

$$\frac{p_i^2}{2m_0} = \varepsilon_i \qquad (10.9)$$

in principle we may use the relations obtained in Sec. 10.2. It is convenient, however, to pass from summation over discrete states to integration because although the states are discrete, they are arranged so close that from the practical viewpoint their distribution may often be considered as continuous. The transition is performed in exactly the same way as was done for a gas of bosons. The following volume falls to one state in momentum space:

$$\Delta\Omega = \Delta p_x \, \Delta p_y \, \Delta p_z = \frac{2\pi\hbar}{a} \frac{2\pi\hbar}{b} \frac{2\pi\hbar}{c} = \frac{(2\pi\hbar)^3}{V} \quad (10.10)$$

where $V = abc$ is the volume in conventional space. We find the number of states whose energy is confined within the interval from ε to $\varepsilon + d\varepsilon$ by dividing the volume $d\Omega$ corresponding to $d\varepsilon$ by $\Delta\Omega$. More exactly, the number of states dG is

$$dG = 2 \frac{d\Omega}{\Delta\Omega} \qquad (10.11)$$

because in each state with a given momentum there may be two electrons differing from each other in the direction of their spin.

The quantity $d\Omega$ is the volume of momentum space confined between p and $p + dp$, so that

$$d\Omega = 4\pi p^2 \, dp$$

If we take (10.9) into consideration, we have

$$d\Omega = 4\pi_t^t (2m_0)^{3/2} \frac{1}{2} \, \varepsilon^{1/2} \, d\varepsilon \qquad \qquad \lceil(10.12)$$

Introduction of (10.10) and (10.12) into (10.11) yields

$$dG = \frac{4\pi \, (2m_0)^{3/2} \, \varepsilon^{1/2} \, d\varepsilon}{(2\pi\hbar)^3} \, V \qquad \qquad \ulcorner(10.13)$$

or

$$dG = g_\varepsilon \, d\varepsilon$$

where the density of states g_ε determining the number of states per unit energy interval, according to (10.13), is

$$g_\varepsilon = \frac{4\pi \, (2m_0)^{3/2} \, \varepsilon^{1/2}}{(2\pi\hbar)^3} \, V \qquad \qquad (10.14)$$

Knowing the density of states, it is a simple matter to go over from sums to integrals. Let $f(\varepsilon)$ be an energy function that does not virtually change within intervals $d\varepsilon$ of the order of kT. Summation over all states may now be performed in two steps. To do this, we divide all possible energy values into intervals of the magnitude $d\varepsilon$ and summate first over states within each interval $d\varepsilon$, and then add up the results obtained. Within one interval, by our assumption, $f(\varepsilon)$ is virtually constant, therefore the result of the first summation is simply the value $f(\varepsilon)$ for this interval multiplied by the number of states dG relating to it. Consequently, summation over the interval $d\varepsilon$ yields

$$f(\varepsilon) \, dG = f(\varepsilon) \, g_e d\varepsilon$$

It is now evident that summation over different intervals consists in evaluating the integral

$$\int f(\varepsilon) \, g_\varepsilon \, d\varepsilon$$

The rule for transition from sums to an integral can be written finally as follows:

$$\sum_i f(\varepsilon_i) \rightarrow \int f(\varepsilon) \, g_\varepsilon \, d\varepsilon$$

For the omega-potential of an ideal electron gas having an energy within the interval from ε to $\varepsilon + d\varepsilon$, we thus obtain

$$d\Omega^* = -kT \ln \left[1 + \exp \left(\frac{\mu - \varepsilon}{kT} \right) \right] g_\varepsilon \, d\varepsilon$$

$$= -kT \ln \left[1 + \exp \left(\frac{\mu - \varepsilon}{kT} \right) \right] \frac{4\pi \, (m_0)^{3/2} \, \varepsilon^{1/2}}{(2\pi\hbar)^3} \, V \, d\varepsilon \quad (10.15)$$

and for the total omega-potential of all the electrons, we have

$$\Omega^* = \int \, d\Omega^* = - \int_0^\infty kT \ln \left[+ \exp \left(\frac{\mu - \varepsilon}{kT} \right) \right] g_\varepsilon \, d\varepsilon$$

Let us introduce the new integration variable $\xi = \varepsilon/(kT)$. Hence,

$$\Omega^* = \frac{(kT)^{5/2} \, 4\pi \, (2m_0)^{3/2}}{(2\pi\hbar)^3} \, V \, \mathrm{erf} \, (\xi_0) \quad (10.16)$$

where $\xi_0 = \mu/(kT)$, and the function $\mathrm{erf} \, (\xi_0)$ is

$$\mathrm{erf} \, (\xi_0) = \int_0^\infty \ln \left[1 + e^{(\xi_0 - \xi)} \right] \xi^{1/2} \, d\xi \quad (10.17)$$

This function cannot be reduced to elementary ones for all values of the argument, but it is possible to obtain simple formulas that hold for large and small values of the variable ξ_0.

If ξ_0 is a small quantity ($\xi_0 \ll -1$), the exponential is also small, and therefore

$$\ln \left[1 + e^{(\xi_0 - \xi)} \right] \approx e^{(\xi_0 - \xi)}$$

For $\mathrm{erf}(\xi_0)$, we obtain

$$\mathrm{erf} \, (\xi_0) = e^{\xi_0} \int_0^\infty e^{-\xi} \xi^{1/2} \, d\xi = e^{\xi_0} \, \frac{\sqrt{\pi}}{2} \quad (10.18)$$

because

$$\int_0^\infty e^{-\xi} \, \xi^{1/2} \, d\xi = \int_0^\infty e^{-x^2} x \, d \, (x^2) = \int_0^\infty e^{-x^2} \, dx = \frac{\sqrt{\pi}}{2}$$

In the opposite limiting case, when ξ_0 is a large quantity ($\xi_0 \gg 1$), the main contribution to the integral is made by the values of the integrand at $\xi < \xi_0$ because at $\xi > \xi_0$,

we have

$$\ln \left[1 + e^{-(\xi-\xi_0)}\right] \approx e^{-(\xi-\xi_0)} \ll 1$$

On these grounds, we can terminate integration at $\xi = \xi_0$ and disregard unity in comparison with the exponential inside the logarithm. We obtain

$$\text{erf}\,(\xi_0) \simeq \int\limits_0^{\xi_0} \ln\left[e^{(\xi_0-\xi)}\right]\xi^{1/2}\,d\xi = \frac{4}{15}\,\xi_0^{5/2} \qquad (10.19)$$

10.4. Non-Degenerate Electron Gas

It is convenient to continue our investigation of the properties of an ideal electron gas separately for the two limiting cases mentioned above. An ideal gas of fermions for which $\xi_0 \ll -1$, i.e. its chemical potential μ is much smaller than $-kT$, is said to be non-degenerate. Let us consider it in greater detail.

It is not difficult to see that *a non-degenerate gas is a gas obeying classical statistics*. That this is true can be shown in the simplest way by analysing its distribution function. For this purpose, let us find the mean number of electrons whose energy is confined within the interval $d\varepsilon$. According to the general rule, from (10.15) we find that

$$dn = \frac{\partial\,(d\Omega^*)}{\partial\mu} = \frac{1}{\exp\left[(\varepsilon-\mu)/(kT)\right]+1}\,\frac{4\pi\,(2m_0)^{3/2}}{(2\pi\hbar)^3}\,\varepsilon^{1/2}\,d\varepsilon V$$

If $\xi_0 \ll \xi$, then $\mu \ll \varepsilon$, and, consequently, with a good approximation

$$\frac{1}{\exp\left[(\varepsilon-\mu)/(kT)\right]+1} \approx \exp\left(\frac{-\varepsilon+\mu}{kT}\right)$$

$$= \exp\left(\frac{\mu}{kT}\right)\exp\left(-\frac{\varepsilon}{kT}\right)$$

i.e. the Fermi-Dirac distribution transforms into the Maxwell-Boltzmann one that differs in the characteristic exponential dependence on the energy of a state. Consequently,

$$dn = \exp\left(\frac{\mu}{kT}\right)\exp\left(-\frac{\varepsilon}{kT}\right)\frac{4\pi\,(2m_0)^{3/2}}{(2\pi\hbar)^3}\,\varepsilon^{1/2}\,d\varepsilon V \qquad (10.20)$$

Formula (10.20) can also be applied to a small portion dV of the entire volume V, whence for the mean number of par-

ticles in the interval $d\varepsilon$ and in the volume dV, we obtain

$$dn = \exp \frac{\mu}{kT} \exp \left(- \frac{\varepsilon}{kT} \right) \frac{4\pi \, (2m_0)^{3/2}}{(2\pi\hbar)^3} \, \varepsilon^{1/2} \, d\varepsilon \, dV \qquad (10.21)$$

Comparing expression (10.21) with the Maxwell energy distribution function, for which formula (3.32) must be multiplied by the electron concentration n, we obtain the relation between the chemical potential μ and the electron concentration for a non-degenerate gas:

$$\exp \left(\frac{\mu}{kT} \right) \frac{4\pi \, (2m_0)^{3/2}}{(2\pi\hbar)^3} = \frac{2\pi}{(kT)^{3/2} \, (\pi)^{3/2}} \, n \qquad (10.22)$$

or

$$\mu = kT \ln \frac{(2\pi\hbar)^3 \, n}{(2\pi m_0 \, kT)^{3/2} 2} = kT \ln \left[\sqrt{2} \; n\hbar^3 \left(\frac{\pi}{m_0 kT} \right)^{3/2} \right] \quad (10.23)$$

This result could have been obtained without using (3.32), but by simply writing that the total mean number of particles in dV equal to $n \, dV$ is determined by the following integral:

$$n \, dV = dV \int\limits_0^\infty \exp \left(\frac{\mu}{kT} \right) \exp \left(- \frac{\varepsilon}{kT} \right) \frac{4\pi \, (2m_0)^{3/2}}{(2\pi\hbar)^3} \, \varepsilon^{1/2} \, d\varepsilon$$

Evaluation of the latter would again lead to an equation equivalent to (10.22) or (10.23).

Hence, a non-degenerate gas does indeed obey classical statistics.

When may an electron gas be considered as non-degenerate? It follows from the condition $\mu \ll - kT$ with a view to (10.23) that

$$\ln \left[\sqrt{2} \, \hbar^3 \, n \left(\frac{\pi}{m_0 kT} \right)^{3/2} \right] \ll - 1$$

i.e.

$$\sqrt{2} \, \hbar^3 n \left(\frac{\pi}{m_0 kT} \right)^{3/2} \ll 1$$

or in another form

$$n \ll \left(\frac{m_0 kT}{\pi\hbar^2} \right)^{3/2} \frac{2}{\sqrt{2}} \qquad (10.24)$$

Relation (10.24) is a criterion of the non-degeneracy of an electron gas. It shows that classical statistics may be applied

when the concentration of the particles is low and their temperature is sufficiently high. The larger the mass of a particle, the more justified is the use of the Maxwell-Boltzmann distribution. Examples of using the criterion (10.24) are included among the exercises to the present chapter.

Since in the absence of degeneracy an electron gas obeys classical statistics, it is evident that its properties do not differ from those of an ideal monatomic gas. Particularly, the internal energy and the equation of state are determined by formulas (6.16) and (6.2), respectively.

10.5. Degenerate Electron Gas

Let us now turn to the opposite limiting case when $\xi_0 \gg$ $\gg 1$ or, differently, when the chemical potential μ is much larger than kT. *An electron gas satisfying the condition* $\mu \gg kT$ *is said to be degenerate.*

In accordance with formulas (10.16) and (10.19), the omega-potential of a degenerate gas has the form

$$\Omega^* = -\frac{4\pi}{(2\pi\hbar)^3} (2m_0)^{3/2} \frac{4}{15} V\mu^{5/2} \qquad (10.25)$$

According to the general rule (8.38), we obtain the following expression for the equation of state:

$$P = \frac{2}{15} \frac{(2m_0)^{3/2}}{\pi^2\hbar^3} \mu^{5/2} \qquad (10.26)$$

For the internal energy, using (8.36) and taking into account that the temperature is not contained in (10.25), we find

$$U = \Omega^* - \mu \frac{\partial\Omega^*}{\partial\mu} = -\frac{3}{2} \Omega^* = \frac{(2m_0)^{3/2}}{5\pi^2\hbar^3} V\mu^{5/2} \quad (10.27)$$

To obtain an explicit dependence of the pressure and internal energy on the temperature, we must insert into (10.26) and (10.27) the chemical potential expressed in terms of the mean number of particles, the temperature, and the volume. If $\langle N \rangle$ is the mean number of electrons in a system, by (8.33) we have

$$\langle N \rangle = -\frac{\partial\Omega^*}{\partial\mu} = \frac{(2m_0)^{3/2}}{5\pi^2\hbar^3} V\mu^{3/2}$$

consequently,

$$n = \frac{N}{V} = \frac{(2m_0)^{3/2}}{5\pi^2\hbar^3} \mu^{3/2}$$

and, therefore,

$$\mu = \frac{n^{2/3}\,(5\pi^2\hbar^3)^{2/3}}{2m_0} \qquad (10.28)$$

Introducing (10.28) into (10.26) and (10.27), we can find

$$P = \frac{(5\pi^2)^{5/3}\hbar^2}{15\pi^2 m_0}\left(\frac{\langle N\rangle}{V}\right)^{5/3} = \frac{(5\pi^2)^{5/3}\,\hbar^2}{15\pi^2 m_0}\,n^{5/3} \qquad (10.29)$$

and

$$U = \frac{(5\pi^2)^{5/3}\,\hbar^2}{10\pi^2 m_0}\left(\frac{\langle N\rangle}{V}\right)^{5/3} V = \frac{(5\pi^2)^{5/3}\,\hbar^2}{10\pi^2 m_0}\,n^{5/3}V \quad (10.30)$$

Hence, for a degenerate gas, the pressure and volume do not depend on the temperature, and the pressure is inversely proportional to the volume raised to the power 5/3.

By (6.43), the heat capacity at constant volume is

$$C_V = \frac{\partial U}{\partial T}$$

If we apply this formula to a degenerate gas, the heat capacity will equal zero because the internal energy does not depend on the temperature. At the same time, however, for a non-degenerate electron gas, the heat capacity is the same as for any monatomic ideal gas, i.e. in accordance with (6.47), we have

$$C_V = \frac{3}{2}\,\langle N\rangle\,k = \frac{3}{2}\,R\,\frac{M}{\mu_0}$$

Metals contain a large number of free electrons, and from the viewpoint of the classical theory it was a riddle why the experimentally found heat capacity is determined only by the ions of the lattice. Quantum statistics explains this phenomenon quite simply. The electron gas in metals is very degenerate (see Example 1 in the Exercises to this chapter), and its heat capacity is thus close to zero.

Let us now see what the criterion of degeneracy of an electron gas is. From the condition

$$\mu \gg kT$$

with account taken of expression (10.28) for the chemical potential, we find, assuming that $\langle N\rangle/V = n$, where n is the concentration:

$$n^{2/3}\,\frac{(5\pi^2\hbar^3)^{2/3}}{2m_0} \gg kT$$

If we raise both sides of this inequality to the power 3/2 and solve it relative to the concentration, we obtain

$$n \gg \left(\frac{m_0 kT}{\pi \hbar^2} \right)^{3/2} \frac{2^{3/2}}{5 \sqrt{\pi}} \qquad (10.31)$$

The condition (10.31) *is a criterion of the electron gas being degenerate.* A comparison with relation (10.24) shows that to within an insignificant factor close to two, these inequalities are inverted with respect to each other.

In concluding, we shall stop to treat the form of the Fermi-Dirac distribution function for strong degeneracy.
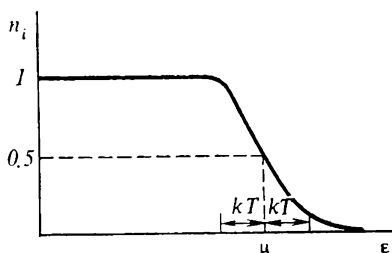
Fig. 10.1

When $\mu \gg kT$, it is good to divide all possible states of the electrons into two groups. For some states in which the energy is much smaller than μ, the mean number of particles $\langle n_i \rangle$ in a given state is virtually equal to unity. Indeed, if the energy ε_i of the state is smaller than μ by at least (2-3) kT, the exponential in the Fermi formula (10.4) has a very small value, and thus $\langle n_i \rangle \approx 1$. Conversely, if a state belongs to the other group so that the energy ε_i is larger than μ by at least several kT's, the exponential is very large and $\langle n_i \rangle$ is close to zero. Hence, in this case the Fermi distribution function has the form shown in Fig. 10.1. It virtually equals unity for all energies lower than μ and zero for all energies larger than μ. There is a comparatively narrow region having a width of the order of $2kT$ in which a change occurs from values near unity to ones near zero. For states having an energy ε_i equal to the chemical potential μ, the mean number of particles $\langle n_i \rangle$ is 1/2. It thus follows that *the chemical potential is the energy of a state whose occupation probability is 1/2.*

10.6. Heat Capacity of Gases with Account Taken of Quantum Effects

The example of an electron gas shows that quantum effects may greatly influence the value of the heat capacity. For instance, with strong degeneracy, the heat capacity of electrons is virtually equal to zero, and only in a non-degenerate electron gas does its value coincide with what is predicted by the classical theory. We already mentioned above that to explain the discrepancies between the classical theory of the heat capacity of gases and experimental results, it is necessary to resort to quantum notions. Let us consider the changes that are obtained here using perhaps somewhat artificial, but, on the other hand, a very simple model allowing us to reveal the essence of the matter.

Assume that we have a rigid diatomic molecule performing plane motion. Since the interatomic spacing is strictly constant, the number of degrees of freedom in such a model is three. Two of them correspond to translational motion in a plane (along the axes x and y), and one to rotation of the molecule relative to an axis perpendicular to the plane (the axis z). According to the classical theory, the internal energy in this case is

$$U = \frac{3}{2} kT \langle N \rangle \qquad (10.32)$$

and the heat capacity is

$$C_N = \frac{3}{2} k \langle N \rangle = \frac{M}{\mu_0} \frac{3}{2} R$$

The main difference between quantum and classical statistics is that account is taken, on the one hand, of the indistinguishability and the Pauli exclusion principles (for fermions), and on the other, of the discreteness of the possible energy values taken on by a system. Let us turn to the model of a molecule performing plane motion. Its energy is the kinetic energy of translational motion along the axes x and y and of rotation relative to the axis z. Let m_0 be the mass of the molecule and I_0 its moment of inertia relative to an axis passing through the centre of mass at right angles to the plane of motion. It is known from mechanics that the total kinetic energy can be represented as the sum of the kinetic energy of translational motion and the kinetic energy

of rotation relative to an axis passing through the centre of mass:

$$\varepsilon = \varepsilon_{\text{trans}} + \varepsilon_{\text{rot}} = \frac{p^2}{2m_0} + \frac{M_z^2}{2I_0} \qquad (10.33)$$

where p is the momentum of a molecule, and M_z is the projection of the angular momentum onto an axis parallel to the z-axis and passing through the centre of mass of the molecule.

The discreteness of the energy values occurs because both the momentum and the angular momentum take on discrete values. As we established in Sec. 7.6, the energy of translational motion is determined by formula (7.23), which in our case of a plane model can be written as

$$\varepsilon_{\text{trans}} = \frac{(2\pi\hbar)^2}{2m_0} \left[\left(\frac{m_x}{a} \right)^2 + \left(\frac{m_y}{b} \right)^2 \right] \qquad (10.34)$$

where a and b are the dimensions of the plane "vessel" along the axes x and y, and m_x and m_y are arbitrary integers. Let us now consider the possible values of the angular momentum. We know from quantum mechanics that the following relation holds for the projection of the angular momentum onto an axis z:

$$M_z = m\hbar \qquad (10.35)$$

where m is an arbitrary integer. The need for relation (10.35) can be explained illustratively, although not strictly, as follows. If a molecule consists of two identical atoms, each of them upon rotating circumscribes a circle of diameter l, where l is the interatomic spacing. Since the latter is constant, in rotation the atoms can be treated as a single particle having their total mass, i.e. that of the molecule. The angular momentum of this particle is

$$M_z = p_{\text{rot}} \frac{l}{2} \qquad (10.36)$$

where p_{rot} is the momentum in rotation in a circle of diameter l. Motion in a circle must be treated as motion in a "vessel" whose length equals that of the circumference, i.e. πl. The possible values of the rotational momentum in such motion in accordance with formulas (7.19) are

$$p_{\text{rot}} = \frac{2\pi\hbar}{\pi l} m \qquad (10.37)$$

where m is an integer. Introducing expression (10.37) into (10.36), we find that the projection of the angular momentum is determined by formula (10.35), i.e. takes on discrete values. It is evident that here the values of the rotational energy

$$\varepsilon_{\text{rot}} = \frac{M_z^2}{2I_0} = \frac{m^2 \hbar^2}{2I_0} \tag{10.38}$$

are also discrete.

Solution of the problem involving the determination of the statistical properties of the model being considered must be commenced with determination of the omega-potential, and for this purpose we must compute the partition function. Taking as a subsystem all the molecules in the state i characterized by a definite set of the numbers m_x, m_y, and m, i.e. having the energy

$$\varepsilon_i = \frac{4\pi^2 \hbar^2}{2m_0 a^2} m_x^2 + \frac{4\pi^2 \hbar^2}{2m_0 b^2} m_y^2 + \frac{\hbar^2}{2I_0} m^2 \tag{10.39}$$

we can write the following expression for the partition function:

$$Z^* = \sum_{n_i} \exp\left(-\frac{\varepsilon_i - \mu}{kT} n_i\right)$$

where n_i is the number of molecules in the state i. A sum of this kind has already been evaluated, and the result depends on what the total spin of the molecule is. If the spin is half-integral, the molecule belongs to fermions, and owing to the Pauli exclusion principle there are altogether two possibilities: $n_i = 0$ and $n_i = 1$. For Z_i^*, we obtain

$$Z_i^* = 1 + \exp\left(\frac{\mu - \varepsilon_i}{kT}\right)$$

If the total spin is integral, the molecule is a boson, and $n_i = 0, 1, \ldots, \infty$. Hence (see Sec. 9.2)

$$Z_i^* = \left[1 - \exp\left(\frac{\mu - \varepsilon_i}{kT}\right)\right]^{-1}$$

For the omega-potential of the subsystem, we find, accordingly,

$$\Omega_i^* = -kT \ln Z_i = -kT \ln\left[1 + \exp\left(\frac{\mu - \varepsilon_i}{kT}\right)\right]$$

for molecules that are fermions, and

$$\Omega_i^* = -kT \ln Z_i = kT \ln \left[1 - \exp\left(\frac{\mu - \varepsilon_i}{kT} \right) \right]$$

for molecules that are bosons.

When the concentration of the molecules is sufficiently low so that the chemical potential is negative and is much larger than kT in magnitude, the exponential term inside the logarithm in both expressions for the omega-potential is small in comparison with unity, and consequently they both reduce to the same expression

$$\Omega_i^* = -kT \exp\left(\frac{\mu - \varepsilon_i}{kT} \right)$$

The latter coincides with expression (9.7) determining the omega-potential of a system calculated without taking the indistinguishability of the particles into consideration. Let us assess the concentrations at which the above assumption holds. Since the omega-potential in this approximation is the same for both bosons and fermions, we can take advantage of the condition of non-degeneracy of a Fermi gas. Let the mass of the atoms in a molecule equal that of a hydrogen atom $m_H = 1.67 \times 10^{-27}$ kg. It thus follows from (10.24) that at temperatures exceeding 20 K (the hydrogen liquefaction point at standard pressure), the condition of non-degeneracy is observed if the concentration of the molecules is lower than $n = 1.7 \times 10^{28}\,\text{m}^{-3}$. Such a high value of the concentration corresponds to condensed media (liquids and solids) so that the condition of non-degeneracy in a gas may be considered to be complied with. For the omega-potential of the entire system, we obtain

$$\Omega^* = \sum_i \Omega_i^* = -kT \sum_i \exp\left(\frac{\mu - \varepsilon_i}{kT} \right)$$

$$= -kT \exp\left(\frac{\mu}{kT} \right) \sum_i \exp\left(-\frac{\varepsilon_i}{kT} \right)$$

Summation over i practically consists in summation over m_x, m_y, and m, consequently,

$$\Omega^* = -kT \exp\left(\frac{\mu}{kT} \right) \sum_{m_x} \exp\left(-\frac{\alpha m_x^2}{kT} \right)$$

$$\times \sum_{m_y} \exp\left(-\frac{\beta m_y^2}{kT} \right) \sum_{m} \exp\left(-\frac{\gamma m^2}{kT} \right)$$

where by (10.33) and (10.36), we have

$$\alpha = \frac{4\pi^2\hbar^2}{2m_0a^2}, \qquad \beta = \frac{4\pi^2\hbar^2}{2m_0b^2}, \qquad \gamma = \frac{\hbar^2}{2I_0}$$

For our further treatment, it is of importance to give attention to the large difference in the values of the coefficients α, β, and γ. Indeed, the moment of inertia of a molecule equals the sum of the products of the atoms' masses and the square of their distance from the axis of rotation, i.e.

$$I_0 = \frac{m_0l^2}{2}$$

Hence, α and β include the products m_0a^2 and m_0b^2, where a and b are the dimensions of the vessel, while γ includes the product m_0l^2, where l is the interatomic spacing. If the vessel dimensions $a \approx b \approx 10^{-2}$ m, and the interatomic spacing is $l \approx 0.7 \times 10^{-10}$ m, which corresponds to that in a hydrogen molecule, then, considering the mass of an atom equal to that of a hydrogen atom, we obtain the following estimates for the values of the coefficients: $\alpha \approx \beta \approx 7 \times 10^{-37}$ J, and $\gamma \approx 1.4 \times 10^{-21}$ J.

Assume that a gas is at an elevated temperature and that kT is much larger than α, β, and γ. Now all three sums can be reduced approximately to integrals of the same type differing in the value of a parameter (α, β, or γ). Let us consider one of them, for instance over m_x. Bearing in mind that the number m_x takes on values from $-\infty$ to $+\infty$ and that upon passing from one addend to the next one it changes by $\Delta m_x = 1$, we can write

$$\sum_{m_x=-\infty}^{+\infty} \exp\left(-\frac{\alpha m_x^2}{kT}\right) = \sum_{m_x=-\infty}^{+\infty} \exp\left(-\frac{\alpha m_x^2}{kT}\right) \Delta m_x$$

$$\approx \int_{-\infty}^{+\infty} \exp\left(-\frac{\alpha m^2}{kT}\right) dm$$

Using the results of Appendix 2 for determining the value of the obtained integral, we find

$$\sum_{m_x} \exp\left(-\frac{\alpha m_x^2}{kT}\right) \approx \sqrt{\frac{kT}{\alpha}\pi}$$

Consequently, at sufficiently high temperatures, we have

$$\Omega^* \approx -kT\, e^{\mu/(kT)}\, \frac{(\pi kT)^{3/2}}{\sqrt{\alpha\beta\gamma}} \tag{10.40}$$

The mean number of molecules by (8.33) is equal to

$$\langle N \rangle = -\frac{\partial \Omega^*}{\partial \mu} = e^{\mu/(kT)}\, \frac{(\pi kT)^{3/2}}{\sqrt{\alpha\beta\gamma}} \tag{10.41}$$

and the internal energy in accordance with (8.36) is

$$U = \Omega^* - T\,\frac{\partial \Omega^*}{\partial T} - \mu\,\frac{\partial \Omega^*}{\partial \mu} = \frac{3}{2}\, kT\, e^{\mu/(kT)}\, \frac{(\pi kT)^{3/2}}{\sqrt{\alpha\beta\gamma}}$$

or, if we use (10.41),

$$U = \frac{3}{2}\, kT\, \langle N \rangle$$

which is in complete agreement with the derivation of the classical theory resulting in (10.32). What are the temperatures at which all three degrees of freedom of a molecule manifest themselves? Since α and β are much smaller than γ, the condition formulated above is observed if $kT \gg \gamma$. With a view to the numerical value of γ and the Boltzmann constant, we find that the inequality is satisfied at temperatures much higher than T', where

$$T' = \frac{\gamma}{k} = 100 \text{ K}$$

Let us now see what happens at temperatures much smaller than T'. If the temperature is such that $kT \ll \gamma$, but kT is still much larger than α and β, the sums with the parameters α and β do not change their value, while the sum over γ becomes equal to unity. Indeed, at $\gamma \gg kT$, all the terms of the sum except the one in which $m = 0$ are very small, so that with a good accuracy we have

$$\sum_m \exp\left(-\frac{\gamma m^2}{kT}\right) \approx 1$$

The expression for the omega-potential is as follows:

$$\Omega^* = -kT \exp\left(\frac{\mu}{kT}\right)\frac{\pi kT}{\sqrt{\alpha\beta}} \tag{10.42}$$

i.e. it is such as if a molecule has only two degrees of freedom corresponding to translational motion. Hence, at $T \ll$

$\ll T'$, the rotational degree of freedom "freezes out". It is natural that if we calculate the internal energy and the heat capacity with the aid of (10.42), we obtain quantities corresponding to two degrees of freedom:

$$U = kT \langle N \rangle, \qquad C_V = \langle N \rangle k$$

If necessary, we can follow the change in the heat capacity from one extreme value to another. For this purpose, it is sufficient to use the expression for the heat capacity obtained from the omega-potential in which the sum over γ is not replaced with an integral. For the transition region, it is sufficient to take only a few terms into account in the sum ($m = 0, \pm 1, \pm 2$) because the influence of the others is small. It is good practice, however, to conduct such calculations for a more realistic model than the one employed above.

What has been said above allows us to understand the reason why only five degrees of freedom must be taken into account in diatomic molecules, and also in linear, i.e. polyatomic ones in which the atoms are arranged along a single axis, instead of six, as must be done when dealing with nonlinear polyatomic molecules. The matter is that in linear molecules, the moment of inertia relative to the axis on which the atoms lie is very small so that the relevant parameter γ and the temperature T' are very large. Indeed, when a molecule rotates about this axis, the moment of inertia is mainly determined by electrons whose mass is by three orders of magnitude less than that of the nucleus. As regards the contribution of the nuclei themselves, owing to the small radius of a nucleus, which is by four orders of magnitude smaller than that of an atom, their contribution to the moment of inertia about the axis joining the nuclei is by eight orders less than to that relative to the axes perpendicular to this direction.

We can explain in a similar way why the vibrations of the atoms in a molecule relative to one another do not tell at low temperatures. Since the energy of vibrations also takes on discrete values, at the energy kT smaller than the minimum energy needed to generate the vibrations, the probability of their generation is so small that the vibrations do not have to be taken into account in computing the partition functions.

Hence, *the quantum theory makes it possible to explain the functional dependence of the heat capacity on the temperature that corresponds to the experimentally observed course of this dependence.*

Exercises

1. *The concentration of electrons in copper is* 8.5×10^{28} m^{-3}. *Determine whether the electron gas is degenerate or non-degenerate at room temperature. At what temperature does the transition from the degenerate to the non-degenerate state occur at the given concentration?*

Solution. At $T = 300$ K, we have

$$\left(\frac{m_0 kT}{\pi \hbar^2} \right)^{3/2} \frac{2^{3/2}}{5 \sqrt{\pi}} \approx 1.3 \times 10^{25} \text{ m}^{-3}$$

this is much smaller than $n = 8.5 \times 10^{28}$ m^{-3}, therefore the gas is degenerate. The gas becomes non-degenerate at a temperature much higher than the melting and vaporization points of copper.

2. *The measured concentration of the electrons in a gas discharge is* $n = 10^{18}$ m^{-3}, *and their temperature is* 2000 K. *What is the pressure of the electrons?*

Solution. In the given case, the gas is non-degenerate because

$$\left(\frac{m_0 kT}{\pi \hbar^2} \right)^{3/2} \frac{1}{\sqrt{2}} \approx 10^{26} \text{ m}^{-3}$$

which is much larger than the value of the concentration. It thus follows that to calculate the pressure, we may use formula (6.2):

$$P = nkT \approx 3 \times 10^{-2} \text{ Pa}$$

Part IV

STATISTICAL PHYSICS
OF NON-EQUILIBRIUM STATES

Chapter 11

BOLTZMANN EQUATION

11.1. Distribution Function
in a Non-Equilibrium Case

It was shown in Chap. 5 that in classical statistics a complete description of a system in equilibrium is given by the Gibbs distribution (or by the grand canonical distribution when the number of particles in a system varies). In practice, we often have to do with systems that are not in equilibrium, and therefore the question appears as to what is the probability density for them.

Since the investigation of non-equilibrium systems is a very involved task, we shall consider in what follows only an ideal gas, i.e. a collection of particles whose interaction is so weak that it may be disregarded. Each particle of an ideal gas moves independently, and therefore the total distribution function of a system is determined by the distribution function of one particle. To convince ourselves that this is true, it is sufficient to repeat our reasoning set out in Sec. 5.2. Indeed, if f $(\mathbf{r}, \mathbf{p})$ is a distribution function, then

$$\frac{\mathrm{d}n}{N} = \frac{f\,(\mathbf{r},\ \mathbf{p})'\mathrm{d}\tau\,\mathrm{d}\Omega}{N} = \mathrm{d}W\,(\mathbf{r},\ \mathbf{p})$$

is the probability of detecting the particle in the volume $\mathrm{d}\gamma = \mathrm{d}\tau\,\mathrm{d}\Omega$ of mu-space (phase space).

The probability of finding the particle 1 in the volume $\mathrm{d}\gamma_1$ and the particle 2 in $\mathrm{d}\gamma_2$, owing to the motion of the particles being independent, is given by the product of the pro-

babilities, i.e.

$$\mathrm{d}W\,(\mathbf{r_1},\ \mathbf{p_1};\ \mathbf{r_2},\ \mathbf{p_2}) = \mathrm{d}W\,(\mathbf{r_1},\ \mathbf{p_1})\,\mathrm{d}W\,(\mathbf{r_2},\ \mathbf{p_2})$$

$$= f\,(\mathbf{r_1},\ \mathbf{p_1})\,\mathrm{d}\gamma_1 f\,(\mathbf{r_2},\ \mathbf{p_2})\,\mathrm{d}\gamma_2\,\frac{1}{N^2}$$

This reasoning can be continued, giving us the probability density of the entire system:

$$w\,(\mathbf{r_1},\ \mathbf{p_1}\ \ldots\ \mathbf{r_N},\ \mathbf{p_N}) = \frac{1}{N^N}\,f\,(\mathbf{r_1},\ \mathbf{p_1})\ \ldots\ f\,(\mathbf{r_N},\ \mathbf{p_N})$$

Hence, *the main task of the theory of an ideal gas is to establish a non-equilibrium distribution function for a single particle.* Since we have in view a non-equilibrium state, this function differs from the Maxwell-Boltzmann distribution, and we must have a general method allowing us to find unknown distribution functions. Such a method was presented by L. Boltzmann and consists in solving the equation he proposed, known as the **Boltzmann (kinetic) equation**. Before considering the equation for a distribution function, let us turn to a problem from the field of hydrodynamics that will give us a better understanding of the meaning of the Boltzmann equation.

11.2. Continuity Equation

Consider the motion of a gas having the density ρ. If m_0 is the mass of one molecule of the gas, its concentration (the number of molecules per unit volume) is

$$n = \frac{\rho}{m_0}$$

Fig. 11.1 shows a system of coordinates and a mentally separated volume element with the sides $\mathrm{d}x$, $\mathrm{d}y$, and $\mathrm{d}z$. Let us first assume that the gas flows along the y-axis and consider the change in its mass in the separated elementary volume. Since the rate of change in the density of the gas at a given point of space is $\partial\rho/\partial t$, the change in the mass occurring during the time interval $\mathrm{d}t$ can be written as

$$\mathrm{d}M = \frac{\partial\rho}{\partial t}\,\mathrm{d}t\,\mathrm{d}\tau \qquad (11.1)$$

where $d\tau = dx\,dy\,dz$. The mass may increase or diminish only as a result of the amount of gas flowing in through the left-hand face with the coordinate y not being equal to the amount of gas flowing out of the right-hand face with the coordinate $y + dy$. If the velocity of the flow is v_y, during the interval dt the volume of the gas that at the instant t coincides with $d\tau$ is displaced over the distance $v_y\,dt$, and
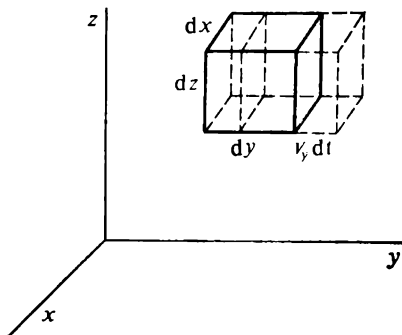
Fig. 11.1

it may be extended or compressed somewhat if the velocities at the right-hand and left-hand faces are not the same. A glance at Fig. 11.1 shows that the amount of gas leaving the volume is

$$\rho v_y\,dt\,dx\,dz = \rho\,(y + dy)\,v_y(y + dy)\,dt\,dx\,dz \qquad (11.2)$$

The volume will be entered from the left by an amount of gas equal to

$$\rho\,(y)\,v_y\,(y)\,dt\,dx\,dz \qquad (11.3)$$

The difference between expressions (11.2) and (11.3) consists in that the values of the density and velocity of the flow at the left-hand face y in the general case do not equal the values of the velocity and the density at the right-hand one $y + dy$. During the time dt, the increase in the mass equals the excess of the inflowing mass in comparison with that flowing out, i.e. the difference

$$\rho\,(y)\,v_y\,(y)\,dt\,dx\,dz - \rho\,(y + dy)\,v_y\,(y + dy)\,dt\,dx\,dz$$

Since y and $y + \mathrm{d}y$ differ by the infinitesimal $\mathrm{d}y$, the same difference can be written as

$$- \frac{\partial}{\partial y} \left[\rho\,(y)\,v_y\,(y) \right] \mathrm{d}y\,\mathrm{d}t\,\mathrm{d}x\,\mathrm{d}z = - \frac{\partial\,(\rho v_y)}{\partial y}\,\mathrm{d}t\,\mathrm{d}\tau \quad (11.4)$$

According to the law of mass conservation, by equating (11.3) and (11.4), we can write

$$\frac{\partial \rho}{\partial t} = - \frac{\partial}{\partial y}\,(\rho v_y)$$

If a gas flow has velocity components along all three axes, reasoning similar to what has been said above will show that the continuity equation has the form

$$\frac{\partial \rho}{\partial t} = - \left[\frac{\partial\,(\rho v_x)}{\partial x} + \frac{\partial\,(\rho v_y)}{\partial y} + \frac{\partial\,(\rho v_z)}{\partial z} \right] \quad (11.5)$$

Dividing both sides of Eq. (11.5) by the mass of one molecule m_0, we find that it can be written in the form of the law of particle number conservation

$$\frac{\partial n}{\partial t} = - \left[\frac{\partial\,(n v_x)}{\partial x} + \frac{\partial\,(n v_y)}{\partial y} + \frac{\partial\,(n v_z)}{\partial z} \right] \quad (11.6)$$

Using the notation adopted in vector analysis, we have

$$\frac{\partial n}{\partial t} = - \operatorname{div}\,(n\mathbf{v}) \quad (11.7)$$

The continuity equation in the form of (11.6) *or* (11.7) *shows that the change in the number of particles in a volume equals the excess of the number of particles flowing into it over the number flowing out.*

11.3. Boltzmann Kinetic Equation

Boltzmann proposed to find the distribution function from an equation similar in meaning to the continuity equation, but written for phase space. Let us recall that in the statistical physics of an ideal gas, the state of a particle is described by setting its three coordinates $(x,\ y,\ z)$ and three momentum components $(p_x,\ p_y,\ p_z)$, i.e. six coordinates of phase space (mu-space according to Sec. 5.2). The distribution function, in accordance with its meaning, must be considered as the concentration of particles in mu-space because the expres-

sion

$$dn = f(\mathbf{r}, \mathbf{p})\, d\gamma$$

determines the mean number of particles in a volume element $d\gamma$ of six-dimensional mu-space.

A change in the number of particles in $d\gamma$ is due to the fact that some of them change their coordinates or the value of the momentum and emerge from $d\gamma$, while others, conversely, arrive into it. Consequently, an equation holds for the distribution function that is similar to the continuity equation, but is written for phase space.

If the position of a particle in phase space is set by the six-dimensional vector $\mathbf{r}_{ph}$ with the components

$$\mathbf{r}_{ph} = \{x, y, z, p_x, p_y, p_z\}$$

the velocity in phase space should be defined as a six-dimensional vector having the components

$$\mathbf{v}_{ph} = \{\dot{x}, \dot{y}, \dot{z}, \dot{p}_x, \dot{p}_y, \dot{p}_z\}$$

where the dot over a symbol stands for its time derivative. Since according to the meaning of the momentum, we have

$$\dot{x} = \frac{p_x}{m_0}, \quad \dot{y} = \frac{p_y}{m_0}, \quad \dot{z} = \frac{p_z}{m_0} \qquad (11.8)$$

and since, by Newton's second laws, we have

$$\dot{p}_x = F_x, \quad \dot{p}_y = F_y, \quad \dot{p}_z = F_z \qquad (11.9)$$

where F_x, F_y, and F_z are the components of the resultant vector of all the forces acting on a particle, the Boltzmann kinetic equation can be written as follows:

$$\frac{\partial f}{\partial t} = -\left[\frac{1}{m_0} \frac{\partial}{\partial x}(fp_x) + \frac{1}{m_0} \frac{\partial}{\partial y}(fp_y) + \frac{1}{m_0} \frac{\partial}{\partial z}(fp_z) \right.$$
$$\left. + \frac{\partial}{\partial p_x}(fF_x) + \frac{\partial}{\partial p_y}(fF_y) + \frac{\partial}{\partial p_z}(fF_z) \right] \qquad (11.10)$$

or with forces not depending on the velocity of the particle,

$$\frac{\partial f}{\partial t} = -\frac{p_x}{m_0}\frac{\partial f}{\partial x} - \frac{p_y}{m_0}\frac{\partial f}{\partial y} - \frac{p_z}{m_0}\frac{\partial f}{\partial z}$$
$$- F_x\frac{\partial f}{\partial p_x} - F_y\frac{\partial f}{\partial p_y} - F_z\frac{\partial f}{\partial p_z} \qquad (11.11)$$

Equation (11.11) can be written in a more condensed form if we use the concept of the **gradient** of a function. The gradient of the function f in conventional space is defined to be a vector whose projections are

$$\text{grad}_r \, f = \left\{ \frac{\partial f}{\partial x}, \; \frac{\partial f}{\partial y}, \; \frac{\partial f}{\partial z} \right\} \tag{11.12}$$

Similarly, the gradient in momentum space is defined to be the vector

$$\text{grad}_p \, f = \left\{ \frac{\partial f}{\partial p_x}, \; \frac{\partial f}{\partial p_y}, \; \frac{\partial f}{\partial p_z} \right\} \tag{11.13}$$

It is not difficult to see that Eq. (11.11) is equivalent to the following one:

$$\frac{\partial f}{\partial t} = -\frac{\mathbf{p}}{m_0} \, \text{grad}_r \, f - \mathbf{F} \, \text{grad}_p \, f \tag{11.14}$$

Equation (11.14) *is known as the* **kinetic equation** *and was proposed by Boltzmann for finding the distribution function* f.

From Eq. (11.11), we can obtain Liouville's theorem, more exactly, a particular case of this theorem relating to six-dimensional mu-space.

The total time derivative of the distribution function, i.e. the derivative calculated with account taken of the change in the coordinates x, y, and z of a particle and in its momentum p_x, p_y, and p_z, in accordance with the law of motion is

$$\frac{\partial f}{\partial t} = \frac{\partial f}{\partial t} + \frac{\partial f}{\partial x} \, \dot{x} + \frac{\partial f}{\partial y} \, \dot{y} + \frac{\partial f}{\partial z} \, \dot{z} + \frac{\partial f}{\partial p_x} \, \dot{p}_x + \frac{\partial f}{\partial p_y} \, \dot{p}_y + \frac{\partial f}{\partial p_z} \, \dot{p}_z$$

If we take into account Eqs. (11.8) and (11.9), it follows from (11.11) that the total derivative is zero:

$$\frac{df}{dt} = 0$$

Assume that N particles are uniformly distributed over a certain volume of phase space $\Delta\gamma$. Hence, the distribution function is non-zero only in $\Delta\gamma$ and there it equals

$$f = \frac{N}{\Delta\gamma}$$

Since $df/dt = 0$, this value is also retained in the region $\Delta\gamma'$ into which particles from $\Delta\gamma$ will pass during the time t.

Therefore, it follows from the condition

$$\frac{N_{\text{s}}}{\Delta\gamma} = \frac{N}{\Delta\gamma'}$$

that

$$\Delta\gamma = \Delta\gamma'$$

i.e. *upon the displacement of a phase volume, its magnitude is conserved.* It is just this statement that is the content of **Liouville's theorem.**

11.4. Interaction with a Heat Bath

In practice, it is more convenient to use an approximate formula instead of the accurate form of the kinetic equation (11.11). To explain the nature of the simplifications used, let us consider, for example, the behaviour of electrons in a gas discharge plasma. Assuming the electron gas to be classical and ideal, we disregard the interaction of the electrons with one another, but take into account the action of external electric fields, and also the interaction with ions and neutral molecules. In the absence of external fields and when the ions and molecules are in an equilibrium state, the electrons are also in equilibrium. Moreover, if the electrons were brought out of their equilibrium state in some way or other, they return to it as a result of collisions with ions and molecules. Hence, the ions and molecules should be considered as a heat bath, interaction with which results in that the system being investigated (the electron gas) arrives at equilibrium characterized by the temperature of the heat bath.

Let us separate from the last term of Eq. (11.14) the part describing interaction with the heat bath, and write

$$\mathbf{F} \operatorname{grad}_p f = \mathbf{F}_{\text{ext}} \operatorname{grad}_p f + \left(\frac{\partial f}{\partial t} \right)_{\text{col}} \qquad (11.15)$$

In (11.15), $\mathbf{F}_{\text{ext}}$ are external forces (for instance, $- e\mathbf{E}$ for electrons in an electric field with the strength $\mathbf{E}$), and $(\partial f/\partial t)_{\text{col}}$ is the symbol used for the result of interaction of the system with the heat bath (for collisions of electrons with neutral molecules and ions). In general, the term $(\partial f/\partial t)_{\text{col}}$ varies depending on what collisions are taken into account, but in one class of cases it can be represented as follows:

$$\left(\frac{\partial f}{\partial t} \right)_{\text{col}} = - \frac{f - f_0}{\tau} \qquad (11.16)$$

where f is a non-equilibrium distribution function, f_0 is an equilibrium distribution function, and τ is a parameter known as the relaxation time.

What considerations suggest such an expression?

First, the collisions must not violate the equilibrium distribution because they are the reason why it sets in. It is a simple matter to see that if $f = f_0$, then $(\partial f/\partial t)_{col} \equiv 0$. Equality to zero occurs for particles having any momentum, therefore relation (11.16) satisfies the detailed balancing principle.

Second, if the deviations from equilibrium are small, we must expect the rate of restoring equilibrium to be proportional to the deviation from the equilibrium state, i.e.

$$\left(\frac{\partial f}{\partial t}\right)_{col} \propto (f - f_0)$$

The relaxation time τ is considered to be known, for example from experiments. Its meaning can be readily understood from the following particular case. Assume that the distribution of particles in space is uniform, but is non-equilibrium as regards the momenta, and there are no external forces. For instance, if under the action of a homogeneous external electric field an electric current flows through a gas, the distribution function is non-equilibrium, but is homogeneous in space, i.e. does not depend on the coordinates. Assume that at the instant $t = 0$ the field is switched off and, consequently, after this the external forces vanish. Since prior to switching off of the field, the distribution function was non-equilibrium, it is evident that in the following too for a certain time it will differ from f_0. For the instants after $t = 0$, the Boltzmann equation is

$$\frac{\partial f}{\partial t} = -\frac{f - f_0}{\tau} \tag{11.17}$$

because the term $(p/m_0)\,\mathrm{grad}_r f$ vanishes since differentiation with respect to the coordinates yields zero (the distribution function is homogeneous), and the term $\mathbf{F}_{ext}\,\mathrm{grad}_p f$ vanishes since the external forces are zero. The solution of Eq. (11.17) is readily found and has the form

$$f(t) = f_0 + [f(0) - f_0]\,e^{-t/\tau} \tag{11.18}$$

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where $f(0)$ is the value of the non-equilibrium distribution function at the initial instant. The quantity

$$\Delta f = [f(0) - f_0]\, e^{-t/\tau} \qquad (11.19)$$

determining the deviation of the distribution function from the equilibrium one diminishes exponentially with the time constant τ which for this reason is called the **relaxation time**. Hence, *a system isolated from external actions violating equilibrium as a result of interaction with a heat bath reaches equilibrium during a time characterized by the relaxation time* τ.

It must be borne in mind that the inclusion of a term of the form of (11.16) into the equation was not performed consistently. Strictly speaking, Boltzmann's method implies that it is necessary to investigate in detail the interaction of an ideal gas with the particles forming the heat bath on the basis of a specific model of the structure of the particles. Expression (11.16) can be justified only if an exact analysis leads to a relation of this kind. Although in some cases this does actually happen (see Chap. 13), quite often matters are different.

Consequently, *the approximate Boltzmann equation taking into account the interaction of the term having relaxation time with a heat bath is*

$$\frac{\partial f}{\partial t} = -\frac{\mathbf{p}}{m_0}\,\mathrm{grad}_r\, f - F_{\mathrm{ext}}\,\mathrm{grad}_p\, f - \frac{f - f_0}{\tau} \qquad (11.20)$$

The widespread use of this form of the equation is explained by its relative simplicity, which makes it possible to represent the solution in an approximate, but not complicated form with a clear physical content. We shall treat only this case in the following.

11.5. Boltzmann Equation with a Quantum-Mechanical Approach

With a strict quantum-mechanical approach, the method of the Boltzmann kinetic equation cannot be applied because the notion itself of the distribution function as a function of the position and momenta of individual particles is inapplicable. The reason underlying this circumstance is very deep and is associated with what is known as the **Heisenberg uncertainty principle** of quantum mechanics accord-

ing to which a particle cannot simultaneously have a definite position (coordinate) and an exact value of its momentum. According to the uncertainty principle, if the position of a particle on the x-axis is established with an accuracy of the order of Δx, its momentum can be known only with an accuracy of Δp_x, and the following relation holds:

$$\Delta p_x \Delta x \gtrsim \pi \hbar \qquad (11.21)$$

Similar uncertainty relations hold for the other axes:

$$\Delta p_y \Delta y \gtrsim \pi \hbar, \qquad \Delta p_z \Delta z \gtrsim \pi \hbar \qquad (11.21')$$

We could explain relations (11.21) to a certain extent by using the method of quantization employed in Chap. 7. Assume that the coordinate x is fixed with the accuracy Δx. We may consider that for this purpose the relevant particle is placed in a potential well whose dimension along the x-axis is Δx. The state of the particle in this case is determined by a standing wave, and the value of the wavelength, i.e. of the momentum, is discrete. A standing wave is the sum of two waves running towards each other with the same amplitudes. This signifies that both a positive and a negative value of the momentum is identically probable in any of the possible states. For the mean-square dispersion of the momentum, we have

$$\langle \Delta p_x^2 \rangle = \langle (p_x - \langle p_x \rangle)^2 \rangle = \langle p_x^2 \rangle$$

because

$$\langle p_x \rangle = \frac{1}{2}\, p_x + \frac{1}{2}\, (-p_x) = 0$$

It is very simple to evaluate the mean value of the square of the momentum, namely,

$$\langle p_x^2 \rangle = \frac{1}{2}\, p_x^2 + \frac{1}{2}\, (-p_x)^2 = p_x^2$$

i.e. the mean-square deviation equals the square of the momentum. Since by formula (7.12), we have

$$p_x = k_x \hbar = \frac{m \pi \hbar}{x}$$

for the quantity $\sqrt{\langle \Delta x^2 \rangle}\, \sqrt{\langle \Delta p_x^2 \rangle}$, we obtain

$$\sqrt{\langle \Delta x^2 \rangle}\, \sqrt{\langle \Delta p_x^2 \rangle} = \Delta x\, \frac{m \pi \hbar}{\Delta x} = m \pi \hbar$$

The uncertainty of the coordinate and momentum is minimum when $m = 1$, and thus we do see that when $\Delta x = \sqrt{\langle \Delta x^2 \rangle}$ and $\Delta p_x = \sqrt{\langle \Delta p_x^2 \rangle}$, we have

$$\Delta x \, \Delta p_x \gtrsim \pi \hbar$$

Hence, in quantum mechanics, the position and momentum of a particle cannot be known exactly at the same time, and, naturally, there is no possibility of describing a system with the aid of a distribution function, which assumes that both the position vector and the momentum of a particle are known. In connection with what has been said above, attention must be drawn to the fact that the Fermi-Dirac and Bose-Einstein quantum distribution functions in this respect differ from the classical ones. Although they do give the mean number of particles in a given state, the quantum-mechanical setting of the state does not imply the simultaneous indication of the momentum and a coordinate.

We can nevertheless also use the classical notion of a distribution function when taking quantum effects into account if we limit ourselves to the **quasiclassical**, i.e. almost classical, approximation in quantum mechanics. In this approximation, the state of a particle is described by both the momentum and a coordinate, but only to the extent allowed by the uncertainty principle. For instance, for one-dimensional motion along the x-axis, a momentum is assigned to a particle with the accuracy Δp_x, where Δp_x is a quantity much smaller than the mean value of the magnitude of the momentum of a system's particles. According to the uncertainty principle, the coordinate cannot be known with an accuracy higher than

$$\Delta x \sim \frac{\Delta p_x}{\pi \hbar}$$

If in a given problem, such an accuracy of setting the coordinate is sufficient, however, we can also speak of the coordinate x. Particularly, such an approach is possible if a particle is in a force field whose potential energy changes so slowly with the coordinate that it should be considered as virtually constant at a distance of the order of Δx. At the same time, such specific quantum features are retained as the discreteness of the momentum and energy values,

the need to take account of the particle indistinguishability principle, and also of the Pauli exclusion principle for particles with a half-integral spin.

If we involve the concept of the density of states introduced in Sec. 7.5, in this approximation a system can be described by the distribution function f $(\mathbf{r}, \mathbf{p})$. Since in the Boltzmann equation, the distribution function signifies the mean number of particles in unit volume of phase space, we must define more precisely what is meant by the equilibrium distribution function f_0 in the term with the relaxation time when it cannot be considered classical.

Let us separate a phase space volume element $\Delta \gamma = = \Delta \tau \, \Delta \Omega$, where $\Delta \tau = \Delta x \, \Delta y \, \Delta z$, and $\Delta \Omega = \Delta p_x \, \Delta p_y \, \Delta p_z$ are so large that they satisfy the uncertainty relations (11.21) and (11.21'), but at the same time are so small that the quasiclassical distribution function in them is virtually constant. The mean number of particles in $\Delta \gamma$ is

$$\langle \Delta N \rangle = \sum \langle n_i \rangle$$

where the sum is evaluated over all states belonging to the selected volume. As was shown in Sec. 7.5, the number of states in $\Delta \gamma$ is expressed by the formula

$$\Delta G = \frac{\Delta \gamma}{(2 \pi \hbar)^3}$$

If the mean number of particles $\langle n_i \rangle$ in any of the states belonging to this volume is virtually the same, we have

$$\langle \Delta N \rangle = \langle n_i \rangle \, \Delta G = \langle n_i \rangle \frac{1}{(2 \pi \hbar)^3} \, \Delta \gamma$$

Hence, the equilibrium distribution function f_0 is

$$f_0 = \frac{\langle \Delta N \rangle}{\Delta \gamma} = \frac{\langle n_i \rangle}{(2 \pi \hbar)^3}$$

or

$$f_0 = \frac{1}{(2 \pi \hbar)^3} \, \frac{1}{\exp \left[(\varepsilon - \mu)/(kT) \right] + 1} \qquad (11.22)$$

for fermions, and

$$f_0 = \frac{1}{(2 \pi \hbar)^3} \, \frac{1}{\exp \left[(\varepsilon - \mu)/(kT) \right] - 1} \qquad (11.23)$$

for a boson gas. *In the relaxation time approximation, a quasiclassical distribution function satisfies the Boltzmann equa-*

tion (11.20), *but in the term accounting for collisions, when taking quantum effects into consideration, the equilibrium Fermi-Dirac distribution function* (11.22) *or the Bose-Einstein function* (11.23) *must be used depending on the type of particles which the gas consists of. The distribution functions* (11.22) *and* (11.23) *relate to particles with a definite value of the spin projection. If the spin of particles is of no importance in a problem, they should be multiplied by the number of possible values of the spin projections* (*two for electrons and two for photons*).

Chapter 12

DISTRIBUTION FUNCTION
IN DIFFUSION APPROXIMATION
(LORENTZ APPROXIMATION)

12.1. Distribution Function with Small Relaxation Time

The Boltzmann kinetic equation, provided that it is solved, gives complete information on the behaviour of an ideal gas. Since the equation even with the simplified term taking collisions into account is still very complicated, it is virtually impossible to obtain a solution for the general case in an analytic form. There is, however, one particular case that is encountered quite often and in which the solution is obtained relatively simply. Let us consider it in greater detail.

The relaxation time in the Boltzmann equation determines the time needed for a system to return to its equilibrium state and characterizes the intensity of interaction of an ideal gas with a heat bath. The stronger the interaction with the heat bath, the smaller is the relaxation time and the more rapidly does the system gain equilibrium. If the external forces are sufficiently small, at a low relaxation time they are not able to violate equilibrium considerably, and the distribution function must be sufficiently close to the equilibrium one. These physical considerations can be given a mathematical form.

Let us rewrite the Boltzmann equation as follows:

$$f = f_0 - \tau \frac{\partial f}{\partial t} - \tau \frac{\mathbf{p}}{m_0} \operatorname{grad}_r f - \tau \mathbf{F}_{\text{ext}} \operatorname{grad}_p f \quad (12.1)$$

When the relaxation time is small, the terms containing τ as a factor are also small, and the distribution function f can be seen to be close to the equilibrium one f_0. Let us introduce into the right-hand side the value of f from the same equation (12.1). We obtain

$$f = f_0 - \tau \frac{\partial f_0}{\partial t} - \tau \frac{\mathbf{p}}{m_0} \operatorname{grad}_r f_0 - \tau \mathbf{F}_{\text{ext}} \operatorname{grad}_p f_0 + O(\tau^2)$$

where $O(\tau^2)$ stands for the terms of the second order of smallness, i.e. proportional to τ^2. They may be dropped. The equilibrium distribution function is independent of the time, so that

$$\frac{\partial f_0}{\partial t} = 0$$

Hence, the non-equilibrium distribution function in this approximation is expressed quite simply in terms of the equilibrium one:

$$f = f_0 - \tau \frac{\mathbf{p}}{m_0} \operatorname{grad}_r f_0 - \tau \mathbf{F}_{\text{ext}} \operatorname{grad}_p f_0 \quad (12.2)$$

The conditions in which the solution (12.2) holds are violated, however, if the varying concentration of the ideal gas in space differs from the equilibrium value. Indeed, in a given small region of space, the equilibrium distribution corresponding to the local concentration sets in very rapidly. At the same time, the equilibrium concentration sets in in the entire volume occupied by the gas by diffusion, i.e. by gradual mixing. This process is quite slow, and therefore representation (12.2), where by f_0 is understood the equilibrium distribution function for the entire gas as a whole, cannot give a good approximation. *The sphere of application of formula* (12.2) *is much broader if we consider it to hold locally, i.e. for relatively small regions of space, and the equilibrium distribution function on the right-hand side is not identical in different regions because it depends on the concentration (or, which is the same, on the chemical potential), that varies from point to point.* Since the law of the change in the concentration is unknown, formula (12.2) cannot

be considered as a solution, at any rate until we find the function $n = n\,(\mathbf{r},\ t)$ or $\mu = \mu\,(\mathbf{r},\ t)$.

We shall consider that owing to effective interaction with the heat bath, the temperature of the ideal gas is constant over the entire volume and equals that of the heat bath. Since now the concentration is not assumed to be constant, the equilibrium distribution function may depend on the time implicitly (in terms of the concentration), so that

$$\tau \frac{\partial f_0}{\partial t} = \tau \frac{\partial f_0}{\partial n}\ \frac{\partial n}{\partial t}$$

In the following when considering the diffusion equation, we shall see that the rate of change in the concentration $\partial n/\partial t$ is a small quantity proportional to τ, so that the term $\tau\,(\partial f_0/\partial t)$ is of the second order of smallness with respect to τ, and although it is non-zero, it nevertheless must be dropped. Problems are sometimes encountered in which the external force $\mathbf{F}_{ext}$ varies rapidly with time. If the rate of its change is characterized by times comparable with the relaxation time τ, the term $\tau\,(\partial f/\partial t)$ must be taken into account, which in this case cannot be replaced with $\tau\,(\partial f_0/\partial t)$. An example of such a situation is the action of infrared radiation on an electron gas in a plasma.

12.2. Diffusion Equation

In a non-equilibrium case, we cannot directly write a function determining the dependence of the particle concentration on the coordinates, but we can obtain an equation known as the **diffusion equation** whose solution determines this relation. In deriving the diffusion equation, we proceed from the Boltzmann equation

$$\frac{\partial f}{\partial t} = - \frac{\mathbf{p}}{m_0}\ \mathrm{grad}_r\, f - \mathbf{F}_{ext}\ \mathrm{grad}_p\, f - \frac{f - f_0}{\tau} \qquad (12.3)$$

Since the concentration of the particles is determined by the relation

$$n\,(\mathbf{r},\ t) = \int f\,(\mathbf{r},\ \mathbf{p},\ t)\ \mathrm{d}\Omega$$

where the integral is evaluated over the entire momentum space, let us attempt to integrate (12.3) over the momenta.

By changing the sequence of integration over the momenta and of time differentiation, it is not difficult to show that

$$\int \frac{\partial f}{\partial t}\, d\Omega = \frac{\partial}{\partial t} \int f\, d\Omega = \frac{\partial n}{\partial t}$$

Let us now consider the result of integration of the term containing the relaxation time (i.e. describing collisions). We have (if τ does not depend on the energy of particles)

$$\int \frac{(f-f_0)}{\tau}\, d\Omega = \frac{1}{\tau} \left(\int f\, d\Omega - \int f_0\, d\Omega \right) = 0$$

Here account is taken of the fact that both integrals equal the same quantity, namely, the local concentration of the particles in the region near the point r. We must note that a zero result is also obtained with much more general assumptions about the term taking collisions into account. Indeed, it is sufficient for interaction to have a nature such that the total number of particles in a given region of space (an integral over all the momenta) will remain unchanged, i.e. there will be no annihilation nor creation of particles. Hence, the equation

$$\int \left(\frac{\partial f}{\partial t} \right)_{\text{col}} d\Omega = 0$$

may be considered to be observed regardless of the more particular assumptions on the nature of interaction with the heat bath.

Now let us turn to evaluation of the integral

$$\int \mathbf{F}_{\text{ext}}\, \text{grad}_p f\, d\Omega$$

It can be written in greater detail as follows:

$$\int \mathbf{F}_{\text{ext}}\, \text{grad}_p f\, d\Omega = F_{\text{ext}, x} \int \frac{\partial f}{\partial p_x}\, dp_x\, dp_y\, dp_z$$

$$+ F_{\text{ext}, y} \int \frac{\partial f}{\partial p_y}\, dp_x\, dp_y\, dp_z + F_{\text{ext}, z} \int \frac{\partial f}{\partial p_z}\, dp_x\, dp_y\, dp_z$$

because the projections $F_{\text{ext}, x}$, $F_{\text{ext}, y}$, and $F_{\text{ext}, z}$ of the force by assumption do not depend on the velocities and may therefore be removed from the integral. Each of the three integrals is evaluated similarly, and it is therefore

sufficient to consider one of them. We have, for example,

$$\int\limits_{-\infty}^{+\infty} dp_y \int\limits_{-\infty}^{+\infty} dp_z \int\limits_{-\infty}^{+\infty} dp_x \frac{\partial f}{\partial p_x} = \int\limits_{-\infty}^{+\infty} dp_y \int\limits_{-\infty}^{+\infty} dp_z \left(f_{p_x=\infty} - f_{p_x=-\infty}\right)$$

Since the number of particles with an infinitely large value of the momentum projection is zero, we have

$$f_{p_x=\infty} - f_{p_x=-\infty} = 0$$

and, consequently,

$$\int \mathbf{F}_{\text{ext}} \, \text{grad}_p f \, d\Omega = 0$$

The integral that we have not evaluated, i.e.

$$\int -\frac{\mathbf{p}}{m_0} \text{grad}_r f \, d\Omega$$

is transformed as follows by replacing the sequence of differentiation over the coordinates and integration over the momenta:

$$\int -\frac{\mathbf{p}}{m_0} \text{grad}_r f \, d\Omega = -\frac{\partial}{\partial x} \int \frac{p_x}{m_0} f \, d\Omega$$

$$-\frac{\partial}{\partial y} \int \frac{p_y}{m_0} f \, d\Omega - \frac{\partial}{\partial z} \int \frac{p_z}{m_0} f \, d\Omega \qquad (12.4)$$

Each of the above integrals relates to a definite region of space in which the concentration is almost constant so that we may use formula (12.2) for the distribution function. Choosing the first of them for a beginning, we can write

$$\int \frac{p_x}{m_0} f \, d\Omega = \int \frac{p_x}{m_0} f_0 \, d\Omega - \int \frac{p_x}{m_0} \frac{\tau \mathbf{p}}{m_0} \text{grad}_r f_0 \, d\Omega$$

$$-\int \frac{p_x}{m_0} \tau \mathbf{F}_{\text{ext}} \text{grad}_p f_0 \, d\Omega \qquad (12.5)$$

Let us now consider consecutively the integrals on the right-hand side of (12.5). We have

$$\int \frac{p_x}{m_0} f_0 \, d\Omega = 0$$

because this integral has the meaning of the mean value of the x velocity component in the equilibrium state described by the distribution function f_0. Formally, the equality to

zero follows from the odd parity of the integrand with respect to p_x.

Let us transform the second integral, which can be represented in the following form:

$$\int \frac{p_x}{m_0} \frac{\tau \mathbf{p}}{m_0} \operatorname{grad}_r f_0 \, d\Omega = \int \frac{p_x^2 \tau}{m_0^2} \frac{\partial f_0}{\partial x} \, d\Omega$$

$$+ \int \frac{p_x p_y \tau}{m_0^2} \frac{\partial f_0}{\partial y} \, d\Omega + \int \frac{p_x p_z \tau}{m_0^2} \frac{\partial f_0}{\partial z} \, d\Omega \qquad (12.6)$$

Of the three integrals on the right-hand side, the last two vanish because the integrand is odd, for example, with respect to p_x. The integral

$$\int \frac{p_x^2 \tau}{m_0^2} \frac{\partial f_0}{\partial x} \, d\Omega$$

remains. Since $p_x^2/m_0^2 = v_x^2$, and the dependence on the coordinate is contained in the integral in terms of the concentration n, of which f_0 is a function, we can write

$$\int \frac{p_x^2 \tau}{m_0^2} \frac{\partial f_0}{\partial x} \, d\Omega = \int v_x^2 \tau \frac{\partial f_0}{\partial n} \, d\Omega \frac{\partial n}{\partial x} = D_x \frac{\partial n}{\partial x} \qquad (12.7)$$

where

$$D_x = \int v_x^2 \tau \frac{\partial f_0}{\partial n} \, d\Omega = \frac{\partial}{\partial n} \int v_x^2 \tau f_0 \, d\Omega$$

The quantity D_x is known as the **diffusion coefficient**.

Let us consider, finally, the last integral in (12.5):

$$\int \frac{p_x}{m_0} \tau \mathbf{F}_{\text{ext}} \operatorname{grad}_p f_0 \, d\Omega = \int \frac{p_x}{m_0} \tau F_{\text{ext}, x} \frac{\partial f_0}{\partial p_x} \, d\Omega$$

$$+ \int \frac{p_x}{m_0} \tau F_{\text{ext}, y} \frac{\partial f_0}{\partial p_y} \, d\Omega + \int \frac{p_x}{m_0} \tau F_{\text{ext}, z} \frac{\partial f_0}{\partial p_z} \, d\Omega$$

Again owing to odd parity of the integrand, the last two integrals vanish. Since the force does not depend on the momentum, we have

$$\int \frac{p_x}{m_0} \tau F_{\text{ext}, x} \frac{\partial f_0}{\partial p_x} \, d\Omega = F_{\text{ext}, x} \int \frac{p_x \tau}{m_0} \frac{\partial f_0}{\partial p_x} \, d\Omega$$

Let us apply the name **drift coefficient** to the quantity

$$\eta_x' = -\frac{1}{n} \int \frac{p_x \tau}{m_0} \frac{\partial f_0}{\partial p_x} \, d\Omega \qquad (12.8)$$

hence

$$\int \frac{p_x \tau}{m_0} F_{\text{ext}, x} \frac{\partial f_0}{\partial p_x} \, d\Omega = - \eta'_x F_{\text{ext}, x} n$$

Gathering all the results obtained, we can write for (12.5)

$$\int \frac{p_x}{m_0} f \, d\Omega = - D_x \frac{\partial n}{\partial x} + \eta'_x F_{\text{ext}, x} n \qquad (12.9)$$

Absolutely identical calculations lead to similar expressions for the other two integrals in (12.4), namely,

$$\left. \begin{array}{l} \int \dfrac{p_y}{m_0} f \, d\Omega = - D_y \dfrac{\partial n}{\partial y} + \eta'_y F_{\text{ext}, y} n \\[2mm] \int \dfrac{p_z}{m_0} f \, d\Omega = - D_z \dfrac{\partial n}{\partial z} + \eta'_z F_{\text{ext}, z} n \end{array} \right\} \qquad (12.9')$$

where

$$\left. \begin{array}{c} D_y = \dfrac{\partial}{\partial n} \displaystyle\int \dfrac{p_y^2 \tau}{m_0^2} f_0 \, d\Omega, \quad D_z = \dfrac{\partial}{\partial n} \displaystyle\int \dfrac{p_z^2 \tau}{m_0^2} f_0 \, d\Omega \\[4mm] \eta'_y = - \dfrac{1}{n} \displaystyle\int \dfrac{p_y \tau}{m_0} \dfrac{\partial f_0}{\partial p_y} \, d\Omega \\[4mm] \eta'_z = - \dfrac{1}{n} \displaystyle\int \dfrac{p_z \tau}{m_0} \dfrac{\partial f_0}{\partial p_z} \, d\Omega \end{array} \right\} \qquad (12.10)$$

Since f_0 and τ depend only on the magnitude of the momentum, we can see that

$$D_x = D_y = D_z \quad \text{and} \quad \eta'_x = \eta'_y = \eta'_z$$

because these integrals are transformed into one another by redesignation of the integration variables. In the following, we shall designate the diffusion coefficient by D, and the drift coefficient by η'.

Hence, the equation of diffusion can be written as

$$\frac{\partial n}{\partial t} = - \frac{\partial}{\partial x} \left[- D \frac{\partial n}{\partial x} + \eta' n F_{\text{ext}, x} \right]$$

$$- \frac{\partial}{\partial y} \left[- D \frac{\partial n}{\partial y} + \eta' n F_{\text{ext}, y} \right] - \frac{\partial}{\partial z} \left[- D \frac{\partial n}{\partial z} + \eta' n F_{\text{ext}, z} \right]$$

$$(12.11)$$

or, using the abbreviated notation of vector analysis,

$$\frac{\partial n}{\partial t} = - \operatorname{div} \left[- D \operatorname{grad} n + \eta' n \mathbf{F}_{\text{ext}} \right] \qquad (12.12)$$

When a gas of charged particles (electrons) is being considered on which an external electric field **E** acts with the force

$$\mathbf{F}_{\text{ext}} = e\mathbf{E}$$

(e is the charge of a particle), instead of the drift coefficient η' introduced above, the concept of the **mobility coefficient** is used. The mobility η is

$$\eta = \eta' e \qquad (12.13)$$

The customarily used form of writing the diffusion equation for electrons is as follows:

$$\frac{\partial n}{\partial t} = -\operatorname{div}\left[-D\operatorname{grad} n + \eta n\,\mathbf{E}\right] \qquad (12.14)$$

Let us consider the value of the coefficients D and η in the diffusion equation. If a gas is non-degenerate, i.e. obeys Maxwell statistics, the diffusion coefficient

$$D = \frac{\partial}{\partial n}\int\frac{p_x^2\tau}{m_0^2}\,\frac{n}{(2\pi m_0 kT)^{3/2}}\,\exp\left(-\frac{p^2}{2m_0 kT}\right)d\Omega$$

$$=\int\frac{p_x^2\tau}{m_0^2}\,\frac{1}{(2\pi m_0 kT)^{3/2}}\,\exp\left(-\frac{p^2}{2m_0 kT}\right)d\Omega = \frac{\langle p_x^2\tau\rangle}{m_0^2} = \langle v_x^2\tau\rangle$$

does not depend on the concentration. As has been established above,

$$\langle v_x^2\tau\rangle = \langle v_y^2\tau\rangle = \langle v_z^2\tau\rangle$$

therefore, taking into account that

$$\langle v^2\tau\rangle = \langle(v_x^2 + v_y^2 + v_z^2)\,\tau\rangle = \langle v_x^2\tau\rangle + \langle v_y^2\tau\rangle + \langle v_z^2\tau\rangle$$

we can write the expression for the diffusion coefficient as follows:

$$D = \frac{1}{3}\langle v^2\tau\rangle \qquad (12.15)$$

In a non-degenerate electron gas, the mobility also does not depend on the concentration:

$$\eta = -\frac{e}{n}\int\frac{p_x\tau}{m_0}\,\frac{n}{(2\pi m_0 kT)^{3/2}}\,\frac{\partial}{\partial p_x}\exp\left(-\frac{p^2}{2m_0 kT}\right)d\Omega$$

$$= -e\int\frac{p_x\tau}{m_0}\,\frac{1}{(2\pi m_0 kT)^{3/2}}\,\frac{\partial}{\partial p_x}\exp\left(-\frac{p^2}{2m_0 kT}\right)d\Omega \qquad (12.16)$$

After performing differentiation of the exponential, we obtain the following expression inside the integral:

$$\eta = \frac{e}{kT} \int \frac{p_x^2 \tau}{m_0^2} \frac{1}{(2\pi m_0 kT)^{3/2}} \exp\left(-\frac{p^2}{2m_0 kT}\right) d\Omega$$

A comparison with (12.16) shows that

$$\eta = \frac{e}{kT} D \qquad (12.17)$$

Expression (12.17) *relating the diffusion coefficient and the mobility of particles obeying classical statistics is known as the* **Einstein equation.**

For particles obeying quantum statistics, the above equations do not hold, and the very concept of the coefficients of diffusion and mobility loses its meaning. We shall explain this statement using as an example a greatly degenerate Fermi gas.

For great degeneracy, the distribution function according to Sec. 10.5 has the form (see Fig. 10.1)

$$f_0 = \left\{ \begin{array}{ll} \dfrac{2}{(2\pi\hbar)^3} & \text{when} \quad \mu < \eta \\ 0 & \text{when} \quad \mu > \eta \end{array} \right\} \qquad (12.18)$$

where the Fermi level μ is determined by Eq. (10.28)

$$\mu = n^{2/3} \frac{(5\pi^2\hbar^3)^{2/3}}{2m_0} \qquad (12.19)$$

Hence, we can write for the diffusion coefficient that

$$D = \frac{\partial}{\partial n} \int \frac{p_x^2 \tau}{m_0^2} f_0 \, d\Omega = \frac{\partial}{\partial n} \int v_x^2 \tau f_0 \, d\Omega$$

If we use the condition $\langle v_x^2 \tau \rangle = \frac{1}{3} \langle v^2 \tau \rangle$, we have

$$D = \frac{1}{3} \cdot \frac{\partial}{\partial n} \int v^2 \tau f_0 4\pi p^2 \, dp$$

where account has been taken of the fact that with an integrand depending on the magnitude of the momentum, $d\Omega = 4\pi p^2 \, dp$.

It is expedient to go over to integrals over the energies. Since

$$\varepsilon = \frac{p^2}{2m_0} = \frac{m_0 v^2}{2}$$

then, taking into account the specific form of the distribution function (12.18), we obtain the following expression for the diffusion coefficient:

$$D = \frac{1}{3} \frac{\partial}{\partial n} \int_0^\mu \frac{2\varepsilon}{m_0} \tau \frac{2}{(2\pi\hbar)^3} 4\pi \sqrt{2} \, m_0^{3/2} \varepsilon^{1/2} \, d\varepsilon \quad (12.20)$$

It will be shown in Chap. 13 that the relaxation time is generally a power function of the energy of an electron:

$$\tau = a\varepsilon^r \quad (12.21)$$

where a and r are constants. After introducing (12.21) into (12.20) the integral is evaluated simply:

$$D = \frac{\partial}{\partial n} \left(\frac{2\sqrt{2}\sqrt{m_0}}{3\pi^2\hbar^3} a \frac{\mu^{r+5/2}}{r+5/2} \right) \quad (12.22)$$

Since the Fermi level depends on the concentration, we have

$$D = \frac{\partial}{\partial \mu} \left(\frac{2\sqrt{2}\sqrt{m_0}}{3\pi^2\hbar^3} a \frac{\mu^{r+5/2}}{r+5/2} \right) \frac{\partial \mu}{\partial n}$$

$$= \frac{2\sqrt{2}\sqrt{m_0}}{3\pi^2\hbar^3} a\mu^{r+3/2} \frac{\partial \mu}{\partial n} \quad (12.23)$$

Introducing μ from (12.19), we find that the diffusion coefficient depends on the concentration by the formula

$$D = Cn^{2(r+1)/3} \quad (12.24)$$

where C is a constant equal to

$$C = \frac{2\sqrt{2}\sqrt{m_0}}{3\pi^2\hbar^3} a \frac{2}{3} \frac{(5\pi^2\hbar^3)^{2/3}}{2m_0} = \frac{2\sqrt{2}\,5^{2/3}}{9} \frac{a}{\pi^{2/3}\sqrt{m_0}\,\hbar} \quad (12.25)$$

Instead of speaking of a diffusion coefficient depending on the concentration, it is better not to introduce such a concept at all, but simply to consider a non-linear transport equation, in the same way as in electrical engineering problems when the resistance of a circuit depends on the current, it is better to speak not of the resistance, but of the non-linear volt-ampere characteristic.

Similarly, for strong degeneracy, after integration by parts (it being taken into account that when $p_x = \infty$, $p_x = -\infty$, the distribution function vanishes), we find for

the mobility

$$\eta = -\frac{e}{n} \int \frac{p_x \tau}{m_0} \frac{\partial f_0}{\partial p_x} \, d\Omega = \frac{e}{n} \int f_0 \frac{\partial}{\partial p_x} \left(\frac{p_x \tau}{m_0} \right) d\Omega$$

$$= \frac{e}{n} \int f_0 \left(\frac{\tau}{m_0} + \frac{\partial \tau}{\partial \varepsilon} \frac{p_x^2}{m_0^2} \right) d\Omega = \frac{e}{n} \int f_0 \left(\frac{\tau}{m_0} + \frac{2\varepsilon}{3m_0} \frac{\partial \tau}{\partial \varepsilon} \right) d\Omega$$

If we use the approximation (12.18) and transfer to an integral over the energy, we have

$$\eta = \frac{e}{n} \int_0^\mu \left(\frac{\tau}{m_0} + \frac{2}{3} \varepsilon \frac{\partial \tau}{\partial \varepsilon} \frac{1}{m_0} \right) \frac{4\pi (2m_0)^{3/2}}{(2\pi\hbar)^3} \varepsilon^{1/2} \, d\varepsilon$$

and after introducing (12.21), we obtain

$$\eta = \frac{e}{n} \frac{1}{m_0} \left(1 + \frac{2}{3} r \right) \frac{4\pi (m_0)^{3/2}}{(2\pi\hbar)^3} a \frac{\mu^{r+3/2}}{r+3/2}$$

$$= \frac{e}{n} \frac{2}{3} \frac{\sqrt{2} \sqrt{m_0}}{\pi^2 \hbar^3} a \mu^{r+3/2} \tag{12.26}$$

A comparison of (12.26) with the expression for the diffusion coefficient shows that the Einstein equation is not observed, and instead of it, we have

$$\eta = \frac{3}{2} \frac{eD}{\mu} \tag{12.27}$$

i.e. the ratio of the diffusion coefficient to the mobility depends on the concentration (in terms of μ). Since the mobility depends on the concentration, it is apparently better not to introduce such a characteristic for a greatly degenerate gas.

The diffusion equation (12.14) determines the concentration of particles at various points of space for a constant temperature, but to obtain a unique solution, we must supplement this equation with boundary and initial conditions, i.e. indicate the values of the concentration on the boundary of the region in which it is being determined, and also its values at the initial instant.

12.3. Distribution Function in the Diffusion Approximation

Assume that by solving the diffusion equation, we are able to find the concentration as a position function. This allows us to obtain a final expression for the non-equilibrium

distribution function. Let us consider in greater detail the classical case when f_0 is the Maxwellian distribution function:

$$f_0 = \frac{n}{(2\pi m_0 kT)^{3/2}} \exp\left(-\frac{p^2}{2m_0 kT}\right) \qquad (12.28)$$

By (12.2), we have

$$f = f_0 - \tau \frac{\mathbf{p}}{m_0} \operatorname{grad}_r f_0 - \tau \mathbf{F}_{ext} \operatorname{grad}_p f_0 \qquad (12.29)$$

Since

$$\frac{\partial f_0}{\partial p_x} = \frac{n}{(2\pi m_0 kT)^{3/2}} \left[\exp\left(-\frac{p^2}{2m_0 kT}\right)\right]\left(-\frac{p_x}{m_0 kT}\right) = -\frac{p_x f_0}{m_0 kT}$$

then

$$\operatorname{grad}_p f_0 = -\frac{\mathbf{p} f_0}{m_0 kT}$$

and, consequently,

$$\tau \mathbf{F}_{ext} \operatorname{grad}_p f_0 = -\tau \frac{\mathbf{p} \cdot \mathbf{F}_{ext}}{m_0 kT} f_0 \qquad (12.30)$$

Further,

$$\operatorname{grad}_r f_0 = \frac{\partial f_0}{\partial n} \operatorname{grad}_r n$$

Since from (12.28), we have

$$\frac{\partial f_0}{\partial n} = \frac{f_0}{n} \qquad (12.31)$$

then

$$\tau \frac{\mathbf{p}}{m_0} \operatorname{grad}_r f_0 = \frac{f_0}{n} \frac{\tau}{m_0} (\mathbf{p} \operatorname{grad}_r n) \qquad (12.32)$$

Hence, *for a classical non-equilibrium distribution function in the diffusion approximation, the following expression holds*:

$$f = f_0 - \frac{\tau f_0}{n m_0} \mathbf{p} \operatorname{grad}_r n + \frac{\tau \mathbf{p} \cdot \mathbf{F}_{ext}}{m_0 kT} f_0 \qquad (12.33)$$

where f_0 is the Maxwell distribution function.

Let us use formula (12.33) to calculate the particle flux density. By formula (3.51), the flux density is determined by the equation

$$\mathbf{j} = \int n w_p \frac{\mathbf{p}}{m_0} d\Omega$$

Since according to the definition of the distribution function
$$f = nw_p$$
we have
$$[\mathbf{j} = \int \frac{\mathbf{p}}{m_0} f \, d\Omega \tag{12.34}$$
In the equilibrium case, the flux density vanishes because the integrand is an odd function of the momentum components (f_0 is an even function of p_x, p_y, and p_z). In the non-equilibrium case, matters are already different, and the flux density is non-zero.

If we introduce into (12.34) the expression for the distribution function from (12.33), we obtain

$$\mathbf{j} = \int \frac{\mathbf{p}}{m_0} f_0 \, d\Omega - \int \frac{\mathbf{p}}{m_0} \frac{\tau f_0}{nm_0} \, (\mathbf{p} \operatorname{grad} \mathbf{n}) \, d\Omega$$
$$- \int \frac{\tau \mathbf{p}}{m_0 kT} f_0 \left(\frac{\mathbf{p} \cdot \mathbf{F}_{ext}}{m_0} \right) d\Omega \tag{12.35}$$

The first integral in (12.35) vanishes owing to the odd parity of the integrand. In the other two, it is necessary to write the product of the vectors in the coordinate form, drop the terms of the integrand that are odd with respect to the momentum components, and put the position functions outside the integral. These transformations are similar to the ones we treated in detail in deriving the diffusion equation. After these transformations, we obtain the following expression for the flux:

$$\mathbf{j} = - \int \frac{p^2 \tau}{3nm_0^2} f_0 \, d\Omega \operatorname{grad} n + \int \frac{p^2 \tau f_0}{3nm_0^2 kT} \, d\Omega \, \mathbf{F}_{ext} \, n$$

Using the definition of the diffusion coefficient and of the mobility, we can write
$$\mathbf{j} = -D \operatorname{grad} n + \eta \mathbf{F}_{ext} n \tag{12.36}$$
A glance at (12.36) reveals that a particle flux in the diffusion approximation is determined by two kinetic phenomena (the temperature is constant): diffusion, with the diffusion flux
$$\mathbf{j}_D = -D \operatorname{grad} n$$
depending on the gradient of the concentration, and the drift with a flux
$$\mathbf{j}_\eta = \eta \mathbf{F}_{ext} n$$
proportional to the applied force.

A comparison of the diffusion equation with the continuity equation (11.6) shows that the diffusion equation allows the following physical interpretation: *the change in the number of particles in unit volume in unit time equals the excess of the incoming flux over the outgoing one*, the flux having two components—the drift and the diffusion ones.

If the electric field $\mathbf{E}$ is applied to a gas of charged particles, the drift flux

$$\mathbf{j}_\eta = \eta' ne\mathbf{E} \tag{12.37}$$

appears, or, if we use the definition of the mobility,

$$\mathbf{j}_\eta = \eta n\mathbf{E} \tag{12.38}$$

For the density of a current associated with the motion of charged particles, we can write

$$\mathbf{i} = e\mathbf{j} = -eD \ \text{grad} \ n + e\eta n\mathbf{E} \tag{12.39}$$

Also distinguished are the density of the diffusion current

$$\mathbf{i}_D = -eD \ \text{grad} \ n \tag{12.40}$$

and the density of the drift current

$$\mathbf{i}_\eta = e\eta n\mathbf{E} \tag{12.41}$$

When the medium is homogeneous and the concentration is constant, the diffusion current vanishes. The current density is determined only by the drift and is proportional to the electric field strength:

$$\mathbf{i} = e\eta n\mathbf{E} \tag{12.42}$$

Formula (12.42) is **Ohm's law** in the differential form, which is usually written as

$$\mathbf{i} = \sigma\mathbf{E} \tag{12.43}$$

where σ is the **conductance**. The conductance is determined in terms of the mobility by the expression

$$\sigma = en\eta \tag{12.44}$$

12.4. Fundamental Equations of the Diffusion Approximation

One of the main tasks in studying non-equilibrium states is the calculation of the magnitude of a current appearing in a system. For this purpose, we must know the distribu-

tion function. In the diffusion approximation, however, the classical distribution function of a non-equilibrium state is determined by the general relation (12.33) with whose help the current density is expressed in terms of the concentration of the charged particles and the electric field strength. It is understood here that the diffusion coefficient and the mobility are known. They can be found experimentally or calculated theoretically. For the latter calculation, as can be seen from formulas (12.16) and (12.17), it is sufficient to know the locally equilibrium distribution function f_0.

Hence, in the diffusion approximation for calculating currents, there is no need each time to revert to the distribution function, and it is only essential to know the diffusion coefficient and the mobility, and also the concentration as a function of the position and time. The latter is found by solving the diffusion equation (12.14), which for this reason is a fundamental equation of the diffusion approximation. An important feature of this equation must be borne in mind, however—it includes the electric field strength $\mathbf{E}$. An electric field is determined, on the one hand, by external sources, but on the other, it depends on the distribution of charged particles that contribute to the field. As we learned in Sec. 4.6, the value of $\mathbf{E}$ can be determined by using the method of the self-consistent field, which leads to the following equation [see (4.30), (4.32)]:

$$\nabla^2 \varphi = -\frac{\rho}{\varepsilon \varepsilon_0} = \frac{e}{\varepsilon \varepsilon_0} (n - n_1) \qquad (12.45)$$

or

$$\operatorname{div} \mathbf{E} = -\frac{e}{\varepsilon \varepsilon_0} (n - n_1)$$

Here n is the concentration of negatively charged particles (electrons), and n_1, of positively charged ones. The concentration of the positively charged particles is assumed to be known. If matters are different, then to determine n_1 another diffusion equation must be used, but written for the concentration of the positive particles.

Consequently, *the solution of most problems in the diffusion approximation consists in solving a system of equations that are fundamental ones for this method, namely, diffusion equations in conjunction with equation* (12.45) *for a self-*

consistent field. This system is quite involved from a mathematical viewpoint because it is non-linear (the diffusion equation includes a term with the product of two unknowns — the electric field strength **E** and the particle concentration n).

Exercises

1. *Show that in the diffusion approximation the mean energy of a particle is the same as in the equilibrium state.*
Solution. The mean energy is calculated by the formula

$$\langle \varepsilon \rangle = \frac{1}{n} \int \frac{p^2}{2m_0} f \, d\Omega$$

where expression (12.2) should be used for f. Since the last two terms in (12.2) are odd functions of p_x, p_y, and p_z, and the energy is an even one, they give a zero contribution. Hence,

$$\langle \varepsilon \rangle = \frac{1}{n} \int \frac{p^2}{2m_0} f_0 \, d\Omega$$

Q.E.D.
2. *Write the diffusion equation and the equation of a self-consistent field for the case when all the quantities depend only on the single coordinate x (a one-dimensional problem).*
Solution. The equation of a self-consistent field is

$$\mathrm{div}\, \mathbf{E} = \frac{dE}{dx} = \frac{e}{\varepsilon \varepsilon_0} (n - n_1)$$

For the diffusion equation, we obtain

$$\frac{\partial n}{\partial t} = -\mathrm{div}\,(-D\,\mathrm{grad}\,n - \eta \mathbf{E}n) = D\,\frac{\partial^2 n}{\partial x^2} + \eta E n$$

Chapter 13

COLLISIONS

13.1. Account of Interaction by Collisions

In the preceding chapters in the Boltzmann equation, we used a form with the relaxation time having no strict substantiation for the term taking account of the interaction of the particles being considered with other ones in equilibrium. The task of the present chapter lies in a more consistent treatment of the interaction between particles and,

particularly, in revealing the conditions in which we may use the concept of the relaxation time, and also in evaluating its magnitude. For definiteness, we shall consider electrons that interact with other particles (neutral molecules, charged ions, etc.) representing a heat bath.

Since we treated the theory of non-equilibrium states for systems that are sufficiently rarefied media, interaction with a heat bath should be interpreted as sequential collisions of an electron with other particles. In a rarefied medium, the probability of an electron simultaneously colliding with several other particles is very low. The overwhelming majority of collisions are, as is said, of a binary nature, i.e. an electron interacts only with one particle near which it was at a given instant, while all other particles are far away and their influence may be disregarded. In condensed media, this assumption is violated.

When an electron collides with another particle, the magnitude and direction of its velocity change. The description of this process is the task of mechanics, which we shall consider in this section in greater detail. For brevity, we shall call the particle which an electron collides with a molecule and designate all quantities relating to this particle by the subscript 2, in contrast to the electron, for which we shall use the subscript 1.

First, let us consider some general properties of a collision process. The classical equations of motion for both interacting particles can be written as

$$m_1\ddot{\mathbf{r}}_1 = \mathbf{F}_{21}, \qquad m_2\ddot{\mathbf{r}}_2 = \mathbf{F}_{12} \qquad (13.1)$$

In these equations, representing Newton's second law, no account is taken of the external forces that are very small in comparison with the force of interaction $\mathbf{F}_{12} = -\mathbf{F}_{21}$ appearing upon a collision. Upon interaction, the electron-molecule system may be considered as closed. Recall that the external forces, which play an appreciable role in the intervals between collisions, are taken into consideration in the Boltzmann equation by a separate term.

The treatment of a collision process is appreciably simplified if we introduce new variables, namely, the position vector of the centre of mass of the two-particle system

$$\mathbf{r}_s = \frac{m_1\mathbf{r}_1 + m_2\mathbf{r}_2}{m_1 + m_2} \qquad (13.2)$$

and the position vector of relative motion

$$\mathbf{r}_r = \mathbf{r}_1 - \mathbf{r}_2 \qquad (13.3)$$

Indeed, we know from mechanics that the centre of mass of a closed system moves at a constant velocity so that a collision process does not affect this motion. On the other hand, if we multiply the first of Eqs. (13.1) by m_2, the second by m_1, and subtract the second result obtained from the first one, we have

$$m_1 m_2 \, (\mathbf{r}_1 - \mathbf{r}_2) = m_1 \mathbf{F}_{21} - m_2 \mathbf{F}_{12} = (m_1 + m_2) \, \mathbf{F}_{21}$$

Dividing both sides of this equation by $m_1 + m_2$ and using (13.3), we obtain

$$\frac{m_1 m_2}{m_1 + m_2} \, \ddot{\mathbf{r}}_r = \mathbf{F}_{21} \qquad (13.4)$$

If we assume that the force $\mathbf{F}_{21}$ with which the second particle acts on the first one is central, i.e. depends on the position vector $\mathbf{r}_r$ joining the second particle to the first one, we shall find that the relative motion occurs as if a particle having a certain effective mass

$$m^* = \frac{m_1 m_2}{m_1 + m_2}$$

is moving relative to a fixed centre acting on it with the force $\mathbf{F}_{21}$. The problem reduces to the one of scattering on a fixed centre, i.e. to a simpler one.

When $\mathbf{r}_r$ and $\mathbf{r}_s$ are known, the initial position vectors $\mathbf{r}_1$ and $\mathbf{r}_2$ are found by the formulas

$$\left.
\begin{aligned}
\mathbf{r}_s + \frac{m_2}{m_1 + m_2} \, \mathbf{r}_r &= \frac{m_1 \mathbf{r}_1 + m_2 \mathbf{r}_2}{m_1 + m_2} + \frac{m_2 \, (\mathbf{r}_1 - \mathbf{r}_2)}{m_1 + m_2} = \mathbf{r}_1 \\
\mathbf{r}_s - \frac{m_1}{m_1 + m_2} \, \mathbf{r}_r &= \frac{m_1 \mathbf{r}_1 + m_2 \mathbf{r}_2}{m_1 + m_2} - \frac{m_1 \, (\mathbf{r}_1 - \mathbf{r}_2)}{m_1 + m_2} = \mathbf{r}_2
\end{aligned}
\right\} \qquad (13.6)$$

Let us now consider the scattering of a particle by a fixed centre. In Fig. 13.1, a particle with an effective mass having the momentum $\mathbf{p}$ after a collision flies away at the angle θ to the direction of its initial motion. We shall treat only elastic collisions in which the total kinetic energy of the interacting particles before and after a collision is the same. Since the scattering centre is fixed, it follows from the law of energy conservation that the magnitude of the

momentum of an effective particle after a collision equals its magnitude before the collision. Only the direction of motion changes. The angle of deflection θ depends on the magnitude of the momentum, and also on the parameter ρ known as the **impact parameter**; the latter equals the distance between the original direction of motion and a straight line parallel to it and passing through the scattering centre (Fig. 13.1).

Let us illustrate the relation between the scattering angle θ and the impact parameter by taking the simple
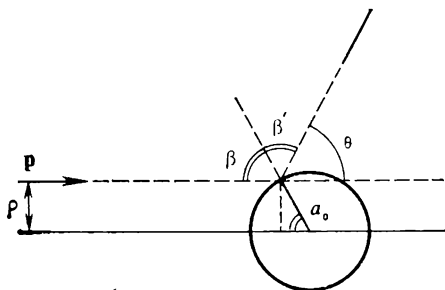
Fig. 13.1

example of the interaction of a point particle with an elastic sphere of radius a_0. Examination of Fig. 13.1 reveals that the angle of incidence β of the particle, equal to the angle of reflection β', is associated with the impact parameter by the relation $a_0 \sin \beta = \rho$. Since it follows from the same figure that $\theta + 2\beta = \pi$, we have

$$\rho = a_0 \sin \beta = a_0 \sin \left(\frac{\pi - \theta}{2} \right) = a_0 \cos \frac{\theta}{2} \qquad (13.7)$$

Hence, the value of the angle of deflection depends on the impact parameter ρ. For a different law of interaction, this relation $\rho = \rho(\theta)$ will naturally be different.

If we change the impact parameter by $d\rho$ the scattering angle will change by $d\theta$, and differentiation yields

$$d\rho = \frac{d\rho(\theta)}{d\theta} d\theta$$

For scattering by a sphere, for instance, we have

$$d\rho = -\frac{a_0}{2} \sin \frac{\theta}{2} d\theta \qquad (13.8)$$

In a gas, any electron that collides with a given molecule may be scattered by it. Assume that we have mentally separated only those electrons for which the magnitudes and directions of the momentum are the same (more exactly, the momentum belongs to an infinitely small interval of values which the volume $d\Omega_1$ corresponds to in momentum space). These electrons fly past the molecule at different
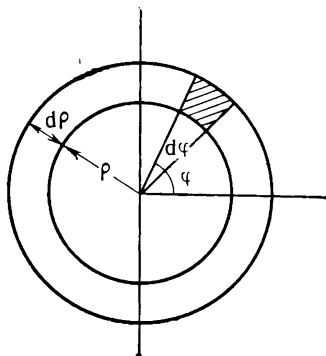
Fig. 13.2

distances from it, and therefore the effective particles may have any impact parameters. Part of the electrons will fly past without virtually deviating from their initial direction, while part of them will be deflected through a definite angle. For the following, it is important to find the fraction of electrons deviating in a given direction.

It is assumed in Fig. 13.2 that the plane of the drawing is normal to the direction of motion. The z-axis passes through the scattering centre in the direction of motion. All the effective particles that pass through the ring depicted in the figure have an impact parameter larger than ρ, but smaller than $\rho + d\rho$, and, consequently, after a collision the direction of their motion will be within an interval of angles from θ to $\theta + d\theta$ with respect to the z-axis. Let us limit ourselves only to the particles that intersect the area hatched in the figure, which corresponds to angles from φ to $\varphi + d\varphi$. The motion of an electron experiencing a collision occurs in one plane, i.e. the angle φ does not change. Hence, particles that have flown through the region hatched

in Fig. 13.2, whose area is

$$ds_0 = \rho \, d\rho \, d\varphi \tag{13.9}$$

will be deflected into the solid angle $d\omega$ characterized by the angles θ to $\theta + d\theta$ with respect to the z-axis parallel to the direction of motion of an oncoming particle, and φ to $\varphi + d\varphi$ in the plane xy. The magnitude of this solid angle is

$$d\omega = \sin \theta \, d\theta \, d\varphi$$

The area ds_0 is called the **differential effective scattering cross section** into the solid angle $d\omega$.

If we use (13.7) and (13.8) in (13.9), we obtain the following expression for scattering by an elastic sphere:

$$ds_0 = - a_0^2 \sin \frac{\theta}{2} \cos \frac{\theta}{2} \frac{1}{2} \, d\theta \, d\varphi = - \frac{a_0^2}{4} \sin \theta \, d\theta \, d\varphi \tag{13.10}$$

Assume that particles with a definite momentum are flying along the z-axis and their flux is j. Hence, the number of particles dN deflected into the solid angle $d\omega$ during the time dt coincides with the number of those of them that have flown during this time through the area ds_0, and, consequently,

$$dN = j \, ds_0 \, dt \tag{13.11}$$

The number of particles deflected through an arbitrary angle is obtained by integration of (13.11) over all possible angles (over φ from 0 to 2π, and over θ from π for a head-on collision to 0 when the particle flies past):

$$N = \int dN = \int j \, ds_0 \, dt = j \, dt \int ds_0$$

The quantity

$$s_0' = \int ds_0 \tag{13.12}$$

is called the **total effective scattering cross section**. For scattering by a sphere, we obtain from (13.10) and (13.12)

$$s_0' = \int_0^{2\pi} d\varphi \int_\pi^0 d\theta \left(- \frac{a_0^2}{4} \right) \sin \theta = \pi a_0^2 \tag{13.13}$$

This result has an obvious geometric meaning because s_0' coincides with the area of the scattering particle visible from the side of the oncoming one. It will be clear from

what follows that it is more convenient to take the quantity
determined by the formula

$$s_0 = \int (1 - \cos \theta) \, ds_0 \qquad (13.14)$$

as the total effective scattering cross section. For the simple
case of scattering by an elastic sphere, the cross section s_0
equals the cross section s_0' because

$$\int \cos \theta \, ds_0 = \int_0^{2\pi} d\varphi \int_\pi^0 \left(-\frac{a_0^2}{4} \right) \sin \theta \cos \theta \, d\theta = 0$$

The mutual motion of an electron and a molecule has an
important feature that can be explained with the aid of
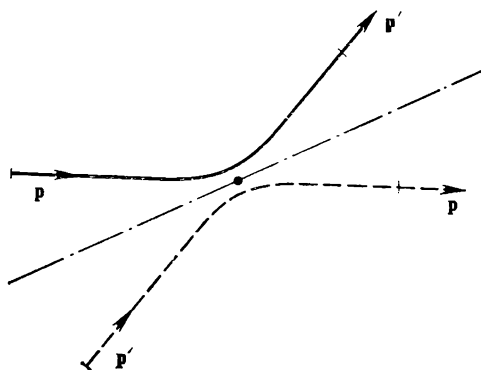
Fig. 13.3

Fig. 13.3. The figure shows the trajectory of relative motion.
The magnitude of the velocity (momentum) is the same at
the beginning and the end of motion. Let us consider the
trajectory depicted by the dashed line in Fig. 13.3. It
corresponds to motion of a particle obtained from the
preceding motion by rotation through 180 degrees about
the axis indicated by the dot-dashed line. The axis has
been drawn through the scattering centre so that it is in
the plane of the trajectory and is inclined identically to the
initial and final portions of the trajectory. With a central
nature of the forces of interaction, it is evident from con-
siderations of symmetry that the dashed trajectory also

corresponds to possible motion. It is also seen that the initial velocity of the second motion coincides in direction and magnitude with the final velocity of the first one, and the final velocity of the second motion, conversely, coincides with the initial velocity of the first motion. It is also obvious from the same considerations of symmetry that the differential scattering cross section is the same for the first and second motions.

Let us now turn to absolute motion. It follows from (13.6) after time differentiation that

$$\mathbf{v_s} + \frac{m_2}{m_1 + m_2}\, \mathbf{v_r} = \mathbf{v_1}; \quad \mathbf{v_s} - \frac{m_1}{m_1 + m_2}\, \mathbf{v_r} = \mathbf{v_2} \quad (13.15)$$

where $\mathbf{v_s}$ is the velocity of the centre of mass of the system, constant in magnitude and direction, $\mathbf{v_r}$ is the velocity of relative motion considered above, and $\mathbf{v_1}$ and $\mathbf{v_2}$ are the velocities of absolute motion. If the initial value of $\mathbf{v_r}$ in the first motion equals the final value of this velocity in the second one, it follows from (13.15) that at the same velocity of the centre of mass, the initial velocities $\mathbf{v_1}$ and $\mathbf{v_2}$ of the first motion equal the final velocities $\mathbf{v_1'}$ and $\mathbf{v_2'}$ of the second because the latter are determined by the relations

$$\mathbf{v_s} + \frac{m_2}{m_1 + m_2}\, \mathbf{v_r'} = \mathbf{v_1'}; \quad \mathbf{v_s} - \frac{m_1}{m_1 + m_2}\, \mathbf{v_r'} = \mathbf{v_2'} \quad (13.16)$$

similar to (13.15).

13.2. Collision Term in the Boltzmann Form

Boltzmann obtained an expression for the term taking into account interaction of particles that holds in a binary collision approximation. The derivation rests on the description of a collision process given in Sec. 13.1. Of significance here is that it additionally takes into consideration the statistical, i.e. random nature of the phenomenon.

Let us separate a volume element $d\tau$ that is much larger than the mean distance between particles, but, on the other hand, is so small that the distribution functions of the electrons and molecules in it do not virtually depend on the coordinates. We shall consider the electrons and molecules whose momenta equal $\mathbf{p_1}$ and $\mathbf{p_2}$, respectively,

or, more exactly, belong to the volume elements $d\Omega_1$ and $d\Omega_2$ of the momentum space. Let us temporarily introduce a system of coordinates (reference frame) that is movable relative to the laboratory and whose origin is at the centre of mass of an arbitrary pair consisting of a colliding electron and a molecule. Since the velocities of all the electrons being considered are equal, like those of the molecules
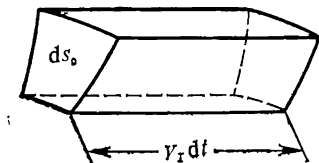
Fig. 13.4

being considered, the centres of mass of the colliding pairs in the new system of coordinates are fixed. Like the pairs themselves, they are distributed uniformly in the volume element $d\tau$.

Let us choose a time interval dt small enough for us to be able to disregard the change in the number of particles in $d\tau$ owing to collisions, but much larger than the duration of a collision itself, and determine the probability of an effective particle that belongs to an arbitrary pair deflecting into the solid angle $d\omega$. The required quantity is at the same time the probability of the effective particle in $d\tau$ passing during the interval dt through the area ds_0 corresponding to scattering into $d\omega$, or, in other words, the probability of the effective particle being (Fig. 13.4) in the body resting on the area ds_0 and having the altitude $v_r \, dt$. It thus equals the ratio of the volume $ds_0 v_r \, dt$ of the body to the volume element $d\tau$.

The mean number of effective particles dN scattered into $d\omega$ can be found by multiplication of the obtained probability and the number of pairs in $d\tau$. If n_1 is the concentration of the electrons, and n_2 is that of molecules, the number of pairs in $d\tau$ equals the number of electrons $n_1 \, d\tau$ multiplied by the number of molecules $n_2 \, d\tau$. Hence, we obtain the following expression for dN:

$$dN = \frac{v_r \, ds_0 \, dt}{d\tau} \, n_1 \, d\tau n_2 \, d\tau = n_1 n_2 v_r \, ds_0 \, dt \, d\tau$$

Since we are considering electrons with momenta belonging to $d\Omega_1$ and molecules with momenta belonging to $d\Omega_2$, we have

$$n_1 = f_1 \, d\Omega_1, \quad n_2 = f_2 \, d\Omega_2$$

so that

$$dN = f_1 f_2 \mid \mathbf{v}_1 - \mathbf{v}_2 \mid ds_0 \, d\Omega_1 \, d\Omega_2 \, dt \, d\tau \qquad (13.17)$$

where it is taken into account that

$$\mathbf{v}_r = \mathbf{v}_1 - \mathbf{v}_2 = \frac{\mathbf{p}_1}{m_1} - \frac{\mathbf{p}_2}{m_2}$$

is the relative velocity of an electron and a molecule. If in (13.17) we treat f_1, f_2 and the relative velocity as functions of the momenta $\mathbf{p}_1$ and $\mathbf{p}_2$ of the electrons and molecules in the initial laboratory coordinate system, then in the differential effective scattering cross section too the angles θ and φ, as well as the magnitude of the relative velocity, must be expressed in terms of parameters characterizing these momenta. The relation between the velocities was obtained in Sec. 13.1 [see (13.15)].

It is quite simple to find the relation between the momentum of an electron $\mathbf{p}_1$ and that of a molecule $\mathbf{p}_2$, on the one hand, and the momentum of the centre of mass $\mathbf{p}_s = \mathbf{v}_s (m_1 + m_2)$ and the momentum of an effective particle $\mathbf{p}_r = m^* \mathbf{v}_r$ on the other. Indeed, if we multiply the first of Eqs. (13.15) by m_1, and the second by m_2, we have

$$\left. \begin{array}{l} \mathbf{p}_1 = m_1 \mathbf{v}_1 = m_1 \dfrac{\mathbf{p}_s}{m_1 + m_2} + \mathbf{p}_r \\[2mm] \mathbf{p}_2 = m_2 \mathbf{v}_2 = m_2 \dfrac{\mathbf{p}_s}{m_1 + m_2} - \mathbf{p}_r \end{array} \right\} \qquad (13.18)$$

With the help of relations (13.18), we can represent expression (13.17) in terms of variables describing the motion of the centre of mass and of an effective particle:

$$dN = f_1 f_2 v_r \, ds_0 \, d\Omega_r \, d\Omega_s \, dt \, d\tau \qquad (13.19)$$

where $d\Omega_r$ and $d\Omega_s$ are volume elements in the momentum space of the effective particles and the centres of mass. It is not difficult to show (see Appendix 4) that the following equality holds:

$$d\Omega_1 \, d\Omega_2 = d\Omega_r \, d\Omega_s \qquad (13.20)$$

It was used in writing (13.19), in which it is also assumed that f_1 and f_2 are represented as functions of $\mathbf{p}_s$ and $\mathbf{p}_r$ with the aid of equations (13.18).

After a collision, the momenta of the electron and the molecule change and become equal to $\mathbf{p}'_1$ and $\mathbf{p}'_2$. The momentum of the centre of mass of the system does not change: $\mathbf{p}'_s = \mathbf{p}_s$ (the law of momentum conservation), while the momentum of an effective particle changes only in direction so that $p'_r = p_r$. If the set of initial momenta was such that the interval of the momenta of the centres of mass
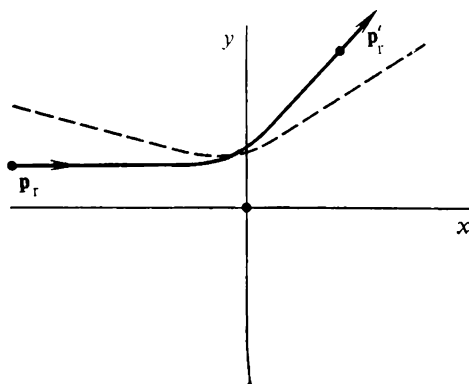
Fig. 13.5

was $d\Omega_s$, then, since each momentum $\mathbf{p}_s$ does not change, the interval $d\Omega'_s$ also remains unchanged so that $d\Omega'_s = d\Omega_s$.

The following reasoning shows that we also have

$$d\Omega'_r = d\Omega_r \tag{13.21}$$

Indeed, although the vector $\mathbf{p}_r$ does not equal the vector $\mathbf{p}'_r$ (its direction has changed), if we change the vector $\mathbf{p}_r$ by $d\mathbf{p}_r$, the momentum after a collision will change by the same magnitude provided that the impact parameter remains the same. It is the simplest to verify this with the aid of Fig. 13.5 that depicts the momenta before and after a collision. We shall change the direction of the initial momentum within a definite interval of angles. With a view to the central symmetry of the interaction potential, we can obtain the same result by leaving the initial vector unchanged

and only turning the initial coordinate system within the same interval of solid angles. It is evident that from the viewpoint of the forces acting in scattering, nothing changes in such turns, therefore the final value of the momentum remains unchanged. But if we consider that what rotates is not the coordinate system, but the initial momentum vector, this signifies that the momentum after a collision turns through exactly the same angles so that its changes equal those in the initial momentum. Hence, $d\mathbf{p}_r = d\mathbf{p}_r'$, and now equality (13.21) follows.

It is thus found that

$$d\Omega_s\, d\Omega_r = d\Omega_s'\, d\Omega_r' \qquad (13.22)$$

Since the momenta after a collision are related by equations (13.18) that are the same as before the collision, we can write in complete analogy with (13.20) that

$$d\Omega_1'\, d\Omega_2' = d\Omega_r'\, d\Omega_s'$$

Comparing this equation with (13.22), we see that the following condition holds:

$$d\Omega_1\, d\Omega_2 = d\Omega_1'\, d\Omega_2' \qquad (13.23)$$

i.e. the product of the momentum space volume elements of the electrons and molecules before a collision equals the corresponding product of the elements after the collision.

Expression (13.19) gives the number of electrons with the momentum $\mathbf{p}_1$ that owing to a collision with molecules having the momentum $\mathbf{p}_2$ acquired the momentum $\mathbf{p}_1'$. In other words, the number of electrons with the momentum $\mathbf{p}_1$ in the volume element $d\tau$ diminished by dN during the time dt, while the number of electrons with the momentum $\mathbf{p}_1'$ increased by the same amount. To take into account the total change in the number of electrons being considered, however, it must be borne in mind that owing to the property of reciprocity noted in Sec. 13.1, the electrons with the momenta $\mathbf{p}_1'$ upon colliding with the molecules having the momenta $\mathbf{p}_2'$ acquire the momenta $\mathbf{p}_1$ and $\mathbf{p}_2$, respectively, after a collision. These transitions play the opposite role relative to the preceding ones. Their number dN' can be evaluated by the same formula (13.17) in which it is obviously necessary to replace all the unprimed variables

with primed ones:

$$dN' = f_1'f_2' \, d\Omega_1' \, d\Omega_2'v_r' \, ds_0' \, d\tau \, dt$$

Hence, the total number of transitions in which the decrease in the number of electrons having the momentum $\mathbf{p}_1$ and of molecules having the momentum $\mathbf{p}_2$ is attended by the relevant increase in the number of electrons having the momentum $\mathbf{p}_1'$ and of molecules having the momentum $\mathbf{p}_2'$ is equal to $dN - dN'$. With a view to Eq. (13.23), and also to the fact that the relative velocities before and after a collision are equal and that with the same impact parameter the differential effective cross sections are the same, we obtain

$$dN - dN' = (f_1f_2 - f_1'f_2') \, d\Omega_1 \, d\Omega_2v_r \, ds_0 \, d\tau \, dt \quad (13.24)$$

For the Boltzmann equation relating to electrons, of interest is the expression determining the diminishing of the number of electrons having the momentum $\mathbf{p}_1$. The molecules with which a collision occurs and the final state of the electrons do not matter. In other words, Eq. (13.24) must be integrated over all possible values of the momenta of the molecules, and also over all final states of the electrons compatible with the initial ones. The latter statement signifies that (13.24) must be integrated over all possible values of the scattering angle. In the Boltzmann equation, the change in the number of electrons is computed for a unit volume of phase space of the initial electrons $d\Omega_1 \, d\tau$ and for a unit time interval dt, so that

$$\left(\frac{\partial f}{\partial t}\right)_{col} = - \int (f_1f_2 - f_1'f_2') \, | \, \mathbf{v}_1 - \mathbf{v}_2 \, | \, ds_0 \, d\Omega_2 \quad (13.25)$$

Expression (13.25) is the Boltzmann term taking into account interaction in the binary collision approximation. The complete Boltzmann equation must be written as

$$\frac{\partial f_1}{\partial t} = - \frac{\mathbf{p}}{m_0} \, \mathrm{grad}_r \, f_1 - \mathbf{F}_{ext} \, \mathrm{grad}_p \, f_1$$

$$- \int (f_1f_2 - f_1'f_2') \, | \, \mathbf{v}_1 - \mathbf{v}_2 \, | ds_0 \, d\Omega_2 \quad (13.26)$$

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where it is assumed that the distribution function of the molecules f_2 is known.

If a system is in equilibrium, collisions do not change its equilibrium state, and the collision term vanishes. Indeed, introducing instead of f_1 and f_2 the equilibrium Maxwell-Boltzmann distribution functions (5.6), we find

$$f_1 f_2 - f_1' f_2' = C_{N1} \exp\left[-\frac{\varepsilon_{n1}(\mathbf{r}) + p_1^2/(2m_{01})}{kT} \right] C_{N2}$$

$$\times \exp\left[-\frac{\varepsilon_{n2}(\mathbf{r}) + p_2^2/(2m_{02})}{kT} \right]$$

$$- C_{N1} \exp\left[-\frac{\varepsilon_{n1}(\mathbf{r}) + p_1'^2/(2m_{01})}{kT} \right] C_{N2}$$

$$\times \exp\left[-\frac{\varepsilon_{n2}(\mathbf{r}) + p_2'^2/(2m_{02})}{kT} \right]$$

$$= C_{N1} C_{N2} \left\{ \exp\left[-\frac{\varepsilon_{n1}(\mathbf{r}) + p_1^2/(2m_{01}) + \varepsilon_{n2}(\mathbf{r}) + p_2^2/(2m_{02})}{kT} \right] \right.$$

$$\left. - \exp\left[-\frac{\varepsilon_{n1}(\mathbf{r}) + p_1'^2/(2m_{01}) + \varepsilon_{n2}(\mathbf{r}) + p_1'^2/(2m_{02})}{kT} \right] \right\} \qquad (13.27)$$

The difference between the two exponentials in braces is zero because the total energies before and after a collision are the same. The equality to zero of the integrand in the collision term expresses the detailed balancing principle according to which forward transitions must be balanced by reverse ones in equilibrium.

In deriving (13.25), the electrons were considered classically, i.e. the electron gas was considered to be non-degenerate. If the concentration of the electrons is high and it is necessary to take into account the indistinguishability and the Pauli exclusion principles, the result differs somewhat. In calculating the probability of scattering of an effective particle into a solid angle, it must be taken into account that the final states into which a transition is performed must be free, i.e. the probability of deflection into the solid angle $d\omega$ must be multiplied by the probability of the final state being free. The latter equals $1 - W$,

where W is the probability of the state being occupied. Since the possible number of fermions in the final state is zero or one, the mean number of particles is determined by the formula

$$\langle n \rangle = 1 \times W + 0 \times (1 - W) = W$$

so that

$$1 - W = 1 - \langle n \rangle$$

From (11.22) and (10.4), we have

$$1 - \langle n \rangle = 1 - (2\pi\hbar)^3 f_{01}$$

A similar relation holds for the non-equilibrium case, except that the equilibrium distribution function must be replaced with the non-equilibrium one:

$$1 - \langle n \rangle = 1 - (2\pi\hbar)^3 f_1$$

An additional factor thus appears in expression (13.17), and the collision term becomes

$$\left(\frac{\partial f}{\partial t}\right)_{\text{col}} = -\int \{f_1 [1 - (2\pi\hbar)^3 f_1'] f_2 - f_1' [1 - (2\pi\hbar)^3 f_1] f_2'\}$$
$$\times |\mathbf{v}_1 - \mathbf{v}_2| \, ds_0 \, d\Omega_2 \qquad (13.28)$$

It is not difficult to show (see the exercise to the present chapter) that the condition of vanishing of the integrand in (13.28) leads to the equilibrium distribution function of electrons being equal to the Fermi-Dirac function.

13.3. Relaxation Time Approximation

To justify the previously used form of the term taking collisions into account, it is necessary to establish the conditions in which the Boltzmann expression (13.25) can be written as

$$\left(\frac{\partial f}{\partial t}\right)_{\text{col}} = -\frac{f_1 - f_0}{\tau} \qquad (13.29)$$

It was found that it is necessary to limit ourselves to elastic (or almost elastic) collisions as a result of which the kinetic

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energy of the colliding particles before a collision equals their kinetic energy after the collision. Although most often, collisions of just this kind play a dominating role, inelastic collisions may also be significant, for instance ones attended by the excitation of molecules causing their subsequent glow (lasers, gas-discharge sources of light, etc.). Account must also be taken of the fact that the mass of a molecule is about four orders of magnitude larger than that of an electron. The result is that the velocities of molecules are much smaller than those of electrons; in an equilibrium state, the root-mean-square value of the velocity is determined by the equation (see Sec. 3.7)

$$v_{\text{rms}} = 1.73 \sqrt{\frac{kT}{m_0}}$$

from which it can be seen that the velocities of molecules owing to their greater mass are two orders less than those of electrons.

When considering collisions in a first approximation, we may consider molecules to be stationary and have an infinite mass. In the course of a collision, the molecule remains at rest, while the electron rebounds with a velocity of the same magnitude (but not of the same direction). The laboratory coordinate system in this approximation coincides with the centre of mass system, all the centres of mass being fixed. Since the velocities (momenta) of the electrons are not associated with the momenta of the molecules, integration over the momenta of the molecules may be performed independently. We have

$$\int f_2 \, d\Omega_2 = \int f_2' \, d\Omega_2 = n_2$$

where n_2 is the concentration of the molecules in the separated volume $d\tau$. The term describing collisions is simplified:

$$\left(\frac{\partial f}{\partial t}\right)_{\text{col}} = -n_2 \mid \mathbf{v}_1 \mid \int (f_1 - f_1') \, ds_0 \qquad (13.30)$$

The magnitude of the velocity of relative motion, equal in the approximation being considered to the magnitude of

the velocity of an oncoming electron, has been put outside the integral because integration over ds_0 actually signifies integration over the scattering angles, and $|\mathbf{v}_1|$ does not depend on them.

If, as we expect, the collision term is reduced to the form of (13.29), the distribution function in the diffusion approximation has the form of (12.33):

$$f_1 = f_{01} + \left[-\frac{\tau f_{01}}{n_1 m_{01}} \, \mathbf{p} \, \mathrm{grad}_r n_1 + \frac{\tau \, (\mathbf{p} \cdot \mathbf{F}_{ext})}{m_{01} kT} \, f_{01} \right] \quad (13.31)$$

or

$$f_1 = f_{01} + \Delta f_1 \tag{13.32}$$

where f_{01} is the equilibrium distribution function, and Δf_1 stands for the non-equilibrium part. The non-equilibrium part of the distribution function can be written as

$$\Delta f_1 = \mathbf{L} \cdot \mathbf{p} f_{01} \tag{13.33}$$

where a comparison with formula (13.31) shows that $\mathbf{L}$ is a vector of the following form:

$$\mathbf{L} = -\frac{\tau}{n_1 m_{01}} \, \mathrm{grad}_r \, n_1 + \frac{\tau \mathbf{F}_{ext}}{m_{01} kT} \tag{13.34}$$

It does not depend on the direction of the momentum of an electron. Substitution of (13.32) into (13.30) yields

$$\left(\frac{\partial f}{\partial t} \right)_{col} = -n_2 \, |\,\mathbf{v}_1\,| \int (f_{01} + \Delta f_1 - f'_{01} - \Delta f'_1) \, ds_0$$

Since the magnitude of the velocity before a collision equals that after the collision, while the equilibrium part of the distribution function depends only on the energy, i.e. on the magnitude of the velocity, we have

$$f_{01} = f'_{01}$$

Hence,

$$\left(\frac{\partial f}{\partial t} \right)_{col} = -n_2 \, |\,\mathbf{v}_1\,| \int (\Delta f_1 - \Delta f'_1) \, ds_0$$

$$= -n_2 \, |\,\mathbf{v}_1\,| \int (\mathbf{L} \cdot \mathbf{p} f_{01} - \mathbf{L} \cdot \mathbf{p}' f'_{01}) \, ds_0$$

$$= -n_2 \, |\,\mathbf{v}_1\,| \, f_{01} \int (\mathbf{L} \cdot \mathbf{p} - \mathbf{L} \cdot \mathbf{p}') \, ds_0 \tag{13.35}$$

where account has been taken of the fact that f_{01} and f'_{01}, like $|\mathbf{v_1}|$, do not depend on the variables over which integration is being performed, and can be removed from the integral.

To complete our calculations, let us consider **Fig. 13.6** which depicts the momenta before and after a collision
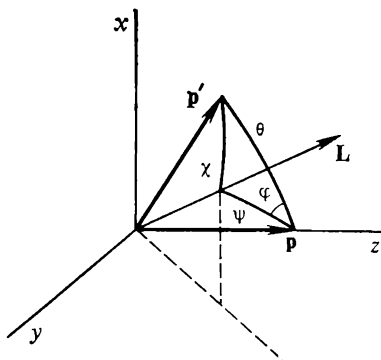
Fig. 13.6

(**p** and **p'**), and also the vector **L**. Retaining the coordinate system that we used in considering the scattering cross section, we draw the z-axis parallel to the vector **p**. The angle between **p** and **p'** is the scattering angle, designated by θ. We shall assume for simplicity that the angle φ equal to zero corresponds to the vector **p'**, i.e. that the x-axis has been chosen in the plane of the vectors **p** and **p'**. The dot (scalar) products $\mathbf{L \cdot p}$ and $\mathbf{L \cdot p'}$ in the integral (13.35) can be written as

$$\mathbf{L \cdot p} = Lp \cos \psi, \quad \mathbf{L \cdot p'} = Lp \cos \chi$$

where ψ and χ are the angles shown in Fig. 13.6, and it has been taken into account that the magnitudes of the momenta **p** and **p'** are the same.

If we draw a spherical surface from the tails of the vectors, the points of its intersection with the vectors form the vertices of a spherical triangle. We can use formulas of spherical trigonometry to express $\cos \chi$ in terms of trigono-

metric functions of the angles θ and ψ, and also of the angle φ equal to that between the planes of the vectors $(\mathbf{p}, \mathbf{p}')$ and $(\mathbf{p}, \mathbf{L})$. According to the cosine law, we have

$$\cos \chi = \cos \psi \cos \theta + \sin \psi \sin \theta \cos \varphi$$

Introducing this value into the integral (13.35), we obtain three terms:

$$\left(\frac{\partial f}{\partial t} \right)_{\text{col}} = - n_2 \mid \mathbf{v}_1 \mid f_{01}$$

$$\times \int (Lp \cos \psi - Lp \cos \psi \cos \theta - Lp \sin \psi \sin \theta \cos \varphi) \, ds_0$$

Integration over ds_0 actually implies integration over the angles θ and φ. Since the last term includes the integral of $\cos \varphi$ with respect to $d\varphi$, it equals zero. Removing $Lp \cos \psi$ from the integral, we obtain

$$\left(\frac{\partial f}{\partial t} \right)_{\text{col}} = - n_2 \mid \mathbf{v}_1 \mid f_{01} Lp \cos \psi \int (1 - \cos \theta) \, ds_0$$

Recalling expression (13.14) for the effective scattering cross section, we shall write

$$\left(\frac{\partial f}{\partial t} \right)_{\text{col}} = - n_2 \mid \mathbf{v}_1 \mid s_0 f_{01} Lp \cos \psi$$

Since in accordance with (13.33), we have

$$f_{01} Lp \cos \psi = f_{01} \mathbf{L} \cdot \mathbf{p} = \Delta f_1$$

then

$$\left(\frac{\partial f}{\partial t} \right)_{\text{col}} = - n_2 \mid \mathbf{v}_1 \mid s_0 \Delta f_1 \tag{13.36}$$

The factor $n_2 \mid \mathbf{v}_1 \mid s_0$ in (13.36) has a dimension that is the reciprocal of time, and we can therefore call the quantity

$$\tau = \frac{1}{n_2 \mid \mathbf{v}_1 \mid s_0} \tag{13.37}$$

the relaxation time. If we now express Δf_1 in terms of f_1

and f_{01} with the aid of (13.32), we can see that (13.36) is equivalent to the expression for the collision term with the relaxation time (11.16). Hence, *if elastic collisions are being considered and the mass of the electrons may be disregarded with a certain approximation in comparison with that of the molecules, the Boltzmann term for collisions is reduced to a form with the relaxation time, the latter being defined as the quantity determined by expression* (13.37).

It must also be noted that in this approximation the collision term containing the relaxation time does not change its form when the electron gas is degenerate. To convince ourselves that this is correct, it is sufficient to write down the expression in braces inside the integral in (13.28), remove the braces, and collect terms. Indeed, since the distribution function f_2 equals f_2' (the energy of the molecules does not change upon collisions with electrons), we have

$$f_1 \left[1 - (2\pi\hbar)^3 f_1' \right] f_2 - f_1' \left[1 - (2\pi\hbar)^3 f_1 \right] f_2'$$
$$= f_2 \left(f_1 - f_1' \right) = f_1 f_2 - f_1' f_2'$$

13.4. Effective Scattering Cross Sections

To determine the relaxation time, we must know the effective scattering cross section s_0. Exact calculations are usually a quite involved task, but it is a simple matter to obtain an estimate of the order of this quantity by using formula (13.13) for an elastic sphere, if we choose its radius a_0 properly.

With Coulomb forces of repulsion, it is reasonable to identify the effective radius with the distance to which an electron and the scattering centre approach each other in a head-on collision. For explanation, let us consider the scattering cross section of an electron by a negative ion. This problem is of interest as applied to both a plasma and to impurity semiconductors. Let the charge of an ion be $-Ze$. If the kinetic energy of an electron at a large distance from the ion is $p_1^2/(2m_1)$, upon a head-on collision the electron will be able to approach the ion to a distance of a_0 determined from the condition that at this distance all the kinetic energy will have transformed into potential energy. Since the potential energy of Coulomb interaction

with an ion is $Ze^2/(4\pi\varepsilon_0 a_0)$, from the condition

$$\frac{p_1^2}{2m_1} = \frac{Ze^2}{4\pi\varepsilon_0 a_0}$$

we obtain the following expression for the effective radius:

$$a_0 = \frac{Ze^2 m_1}{2\pi\varepsilon_0 p_1^2}$$

If we express the momentum in terms of the energy of an oncoming electron, after substitution of the above expression for a_0 in (13.13) we find for the scattering cross section by an ion that

$$s_0 = \frac{Z^2 e^4}{16\pi\varepsilon_0^2\varepsilon_1^2} \qquad (13.38)$$

Hence, the scattering cross section depends on the energy of an electron. In the given case, the larger the energy, the smaller is the cross section, i.e. the less are the electrons scattered. It is interesting to note that such a rough estimate of the cross section is in quite good agreement with a stricter calculation*. Introducing (13.38) into the formula determining the relaxation time and expressing the velocity of an electron in terms of its energy ε_1, we arrive at the following result:

$$\tau = \frac{1}{n_2 s_0 \mid \mathbf{v} \mid} = \frac{16\pi\varepsilon_0^2 \sqrt{m_1}}{n_2 Z^2 e^4 \sqrt{2}} \varepsilon_1^{3/2} \qquad (13.39)$$

This formula is in agreement with the previously assumed relation

$$\tau = a\varepsilon_1^r \qquad (13.40)$$

[(see 12.21)], where $r = 3/2$.

With the aid of (13.39), it will be a simple matter to establish a **temperature dependence of the conductivity** when the dominating role is played by scattering by charged centres. The temperature dependence of the conductivity at a constant concentration of the electrons is determined by the temperature dependence of the mobility or, if we

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* The case of scattering upon Coulomb interaction is a special one, and to obtain the final result with "strict" calculations we have to introduce additional restrictions leading to the appearance of a logarithmic factor whose numerical value does not usually exceed a few units.

have in view the Einstein relation, of the diffusion coefficient D. Since

$$D = \langle v_x^2 \tau \rangle \propto \varepsilon \tau \, (\varepsilon) \propto \varepsilon^{r+1}$$

and the energy of a non-degenerate electron gas is proportional to the temperature, we have

$$\sigma \propto \mu \propto \frac{D}{T} \propto \frac{T^{r+1}}{T} = T^r$$

i.e. in the given case the conductivity grows with elevation of the temperature in proportion to $T^{3/2}$.

Upon the scattering of electrons by neutral molecules in a plasma or by neutral defects in a crystal lattice of a solid
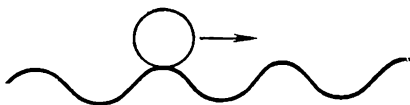
Fig. 13.7

body, a reasonable approximation of the radius of the scattering sphere is the "radius" of the molecule or defect. In this case

$$s_0 = \pi a_0^2$$

and

$$\tau = \frac{1}{n_2 \pi a_0^2 v} = \frac{\sqrt{m_1}}{n_2 \pi a_0^2 \sqrt{2}} \, \varepsilon^{-1/2}$$

i.e. the exponent of ε is $-1/2$. Such a dependence of the relaxation time on the energy leads to a temperature dependence of the conductivity of the kind

$$\sigma \propto T^{-1/2}$$

An important case is the scattering of electrons by the thermal vibrations of a crystal lattice. When an electron is moving along a regular row of crystal lattice atoms whose thermal motion we disregard, it is better to replace the notion of consecutive collisions with a picture of the motion of an electron in the periodic field of potential forces. An illustrative model of such motion is that of a ball over an ideal corrugated surface (like a sheet of corrugated roofing) under the action of the force of gravity (Fig. 13.7). It is

obvious that the ball moves with acceleration, retarding its motion on the ridges and accelerating it in the grooves, but the mean velocity of such motion in the absence of friction forces is constant. This signifies that there is no scattering and the relaxation time is infinite. This time is finite only when ideal periodicity is violated. In real crystals, such violations are associated either with defects of the crystal structure, for instance with the presence of vacant lattice points (vacancies), of atoms in the interstices, with the presence of atoms of a different species (alloys), or with thermal motion resulting in chaotic deflection of the lattice atoms from the position of stable equilibrium at a point. The scattering of an electron in this model consists in that after interaction with a scattering centre it changes the direction and magnitude of its mean velocity.

Let us consider the role of the thermal vibrations of atoms. In an illustrative, although not strict, interpretation, we may assume that the thermal displacement of an atom from its equilibrium position leads to the appearance of a scattering centre with a radius equal to the mean displacement of an atom from its equilibrium position. With small deviations, the interaction of an atom with its neighbours is almost elastic. If we designate the rigidity coefficient of the elastic force by β, deflection over a distance of r will lead to an increase in the potential energy of an atom by $\beta r^2/2$. Since according to the principle of equipartition of energy the mean potential energy of the elastic force is $\frac{3}{2} kT$, for the radius of a neutral scattering centre we obtain

$$a_0 = \sqrt{\langle r^2 \rangle} = \sqrt{\frac{3kT}{\beta}} \qquad (13.41)$$

Having determined the scattering cross section, we find the following expression for the relaxation time:

$$\tau = \frac{\beta}{n_2 \pi 3 k T v} \qquad (13.42)$$

The distinction from the preceding case is that the coefficient a itself at the energy in formula (13.40) depends on the temperature. Therefore, the conductivity is proportional to the temperature raised to the power $-3/2$, and not

—1/2 as in scattering by the neutral defects of a crystal lattice.

For a degenerate electron gas (metals), the mean energy of the electrons does not virtually depend on the temperature, consequently the conductivity is inversely proportional to the temperature in scattering by the thermal vibrations of the lattice and does not depend on the temperature in scattering by neutral defects.

13.5. Free Path

In the binary collision model, the electron moves by inertia or under the action of external forces, and from time to time collides with other particles that are a heat bath (we do not deal with collisions of electrons with one another, limiting ourselves to cases in which they do not
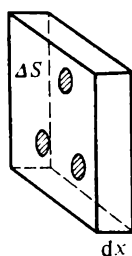
Fig. 13.8

play a significant role). What is the probability of an electron experiencing a collision on a section of its path having a length of dx?

This matter can be solved if we consider the elementary parallelepiped depicted in Fig. 13.8. The face perpendicular to the direction of motion of an electron has the area ΔS while the altitude of the parallelepiped is dx. Let the concentration of molecules be n_2. Hence, the parallelepiped contains on the average $n_2 \, \Delta S \, dx$ molecules. With a scattering cross section of s_0, the total area for the collision of an electron flying through the selected volume in the direction of the x-axis with any of the molecules is $s_0 n_2 \, \Delta S \, dx$. The altitude of the parallelepiped is assumed to be very small, therefore the probability of one molecule "screening"

another one may be ignored. In these conditions, the probability of a collision dW is determined by the ratio of the total area of the molecules to the entire area of the front face of the parallelepiped, i.e.

$$dW = \frac{s_0 n_2 \Delta S\, dx}{\Delta S} = n_2 s_0\, dx$$

The quantity $1/(n_2 s_0)$ has the dimension of length. If we designate it by λ, we have

$$dW = \frac{dx}{\lambda} \tag{13.43}$$

Let us now consider the length interval x and determine the probability of an electron experiencing no collision within this interval. If we divide the entire interval x into intervals each with a length of dx so that the total number of intervals is x/dx, the required probability can be represented as the product of the probabilities of a number of independent events. The probability of an electron experiencing no collision within the interval dx is $1 - dx/\lambda$, therefore the probability of the absence of collisions on the length x is

$$W_{abs} = \left(1 - \frac{dx}{\lambda}\right)^{x/dx} = \left(1 - \frac{x}{\lambda}\frac{dx}{x}\right)^{x/dx}$$

Since x/dx is a large quantity (an infinitely large one in the limit), by using the limit known from mathematics, i.e.

$$\lim_{N\to\infty}\left(1 - \frac{b}{N}\right)^N = e^{-b}$$

we obtain

$$W_{abs} = e^{-x/\lambda} \tag{13.44}$$

Finally, let us find the probability dW' of an electron covering the path x without collisions and experiencing a collision in the interval dx terminating this path. It evidently is

$$dW' = e^{-x/\lambda}\frac{dx}{\lambda} \tag{13.45}$$

We can use expression (13.45) to calculate the mean free path of an electron. According to the general rule for finding

mean values, we write

$$\langle x \rangle = \int\limits_0^\infty x \, \mathrm{d}W' = \int\limits_0^\infty x \mathrm{e}^{-x/\lambda} \, \frac{\mathrm{d}x}{\lambda}$$

Evaluation of the integral yields

$$\langle x \rangle = \lambda \qquad (13.46)$$

so that *the quantity* λ introduced above *has the meaning of the mean distance from an arbitrary point to the point of the next collision.* If we assume that we began to consider the motion of an electron immediately after a collision, then λ *is the mean distance between two consecutive collisions.* This allows us to interpret λ as **the mean free path.**

Returning to formula (13.37) for the relaxation time, we see that it can be represented in the form

$$\tau = \frac{1}{n_2 s_0 v_1} = \frac{\lambda}{v_1} \qquad (13.47)$$

i.e. *the relaxation time has the meaning of the time interval from an arbitrary moment to the instant of the next collision. It can also be interpreted as the mean time between two consecutive collisions.*

Let us finally consider the free path when scattering centres of various kinds are present. If there are molecules of various species (1, 2, 3) with different scattering cross sections s_{01}, s_{02}, s_{03}, the probability of an electron colliding with a molecule in the layer $\mathrm{d}x$ is

$$\mathrm{d}W = n_{21} s_{01} \, \mathrm{d}x + n_{22} s_{02} \, \mathrm{d}x + n_{23} s_{03} \, \mathrm{d}x,$$

or

$$\mathrm{d}W = \frac{\mathrm{d}x}{\lambda_1} + \frac{\mathrm{d}x}{\lambda_2} + \frac{\mathrm{d}x}{\lambda_3} = \left(\frac{1}{\lambda_1} + \frac{\lambda}{\lambda_2} + \frac{1}{\lambda_3} \right) \mathrm{d}x$$

Since expression (13.43) can be treated as a definition of the free path, we have

$$\frac{1}{\lambda} = \frac{1}{\lambda_1} + \frac{1}{\lambda_2} + \frac{1}{\lambda_3} \qquad (13.48)$$

Hence, *when many scattering centres are present, the reciprocal of the mean free path equals the sum of the reciprocals of the free paths in scattering by centres of each kind separately.*

Examination of (13.47) shows that a similar rule also holds for the relaxation time

$$\frac{1}{\tau} = \frac{1}{\tau_1} + \frac{1}{\tau_2} + \frac{1}{\tau_3} \tag{13.49}$$

13.6. Heating of an Electron Gas

The form for the collision term considered in Sec. 13.3 was obtained with the use of an assumption having a short-coming of principle. We have in view the assumption that the mass of a molecule is virtually infinite in comparison with that of an electron. Having adopted it, we cannot explain how electrons in an external electric field retain a constant mean energy in stationary conditions. It is an especially simple matter to convince ourselves that this is true if we consider the molecules to be fixed. Upon each collision, an electron rebounds, retaining the magnitude of its velocity. Since when an external field is present a current flows in the system, this signifies that the electric field does work, increasing the energy of the system of electrons. We must discover how the stationary state is maintained. It is well known that when a current flows in a wire, heat is evolved in it, i.e. energy is transferred to the heat bath. It is obvious that to explain this phenom-enon, we must take into account the transfer of energy from the electrons to the molecules in collisions, i.e. the finite value of the ratio of the mass of a molecule to that of an electron. Since in equilibrium, the transfer of energy from electrons to molecules is compensated by its reverse transmission from the molecules to the electrons, the deci-sive role is played by the unbalanced nature of the electron distribution function. We must bear in mind, however, that the correction to the distribution function found above cannot explain this effect. More probably, the opposite holds, since the current is determined by this correction, it is capable of explaining how the electrons obtain energy, or, in other words, how they get "warmed up". It will be seen from the following that this is how matters actually are. Consequently, the conclusion suggests itself that in the non-equilibrium distribution function (13.31), the function f_{01}, which we considered to be equilibrium, cannot actually be such, and in the best case it is close to equilibrium.

If we assume, for instance, that it is a Maxwellian function, a higher temperature should correspond to it. It is possible, however, that this function is not Maxwellian. The present section is devoted to a solution of this important matter.

We shall begin with the assumption that the required distribution function has the form

$$f_1 = f_{01} + \Delta f_1 \qquad (13.50)$$

and differs from the one used previously only in that f_{01} now does not coincide with the equilibrium distribution function, but also depends on the magnitude of the momentum or on the energy of the electrons. Our task consists in finding this, as it is customarily called, isotropic part of the distribution function. We must naturally proceed from the Boltzmann equation (13.26). If we introduce the distribution function in its assumed form given by (13.50) into the Boltzmann equation, we can write the result as follows:

$$\frac{\partial f_{01}}{\partial t} + \frac{\partial \Delta f_1}{\partial t} = -\frac{\mathbf{p}_1}{m_1} \operatorname{grad}_r f_{01} - \frac{\mathbf{p}_1}{m_1} \operatorname{grad}_r \Delta f_1$$

$$+ e\mathbf{E} \operatorname{grad}_p f_{01} + e\mathbf{E} \operatorname{grad}_p \Delta f_1 + \left(\frac{\partial f_{01}}{\partial t} \right)_{\text{col}} + \left(\frac{\partial \Delta f_1}{\partial t} \right)_{\text{col}}$$
$$(13.51)$$

We shall limit ourselves to a relatively simple case, namely, to a stationary problem in a constant and homogeneous electric field. Since the field does not depend on the time, the stationary solution should be sought by assuming that the terms with time derivatives in (13.51) vanish. For other conditions, for instance when an electron gas is in a varying electric field of sufficiently high frequency, these terms must be taken into account. Homogeneity in space signifies that the distribution function does not depend on the coordinates, therefore the first two terms on the right-hand side of Eq. (13.51) also vanish. The equation becomes

$$- e\mathbf{E} \operatorname{grad}_p f_{01} - e\mathbf{E} \operatorname{grad}_p \Delta f_1 = \left(\frac{\partial f_{01}}{\partial t} \right)_{\text{col}} + \left(\frac{\partial \Delta f_1}{\partial t} \right)_{\text{col}}$$
$$(13.52)$$

If the isotropic part of the distribution function corresponds to equilibrium, the term $(\partial f_{01}/\partial t)_{\text{col}}$ vanishes, and the collision term reduces to $(\partial \Delta f_1/\partial t)_{\text{col}}$. In the relaxation

time approximation, we used the representation (11.16) for the collision term:

$$\left(\frac{\partial \Delta f_1}{\partial t}\right)_{col} = - \frac{\Delta f_1}{\tau}$$

and we assumed [see (12.29), where $\mathbf{F} = -e\mathbf{E}$] that

$$\Delta f_1 = \tau e \mathbf{E} \, \text{grad}_p \, f_{01} = \tau e \mathbf{E} \, \frac{\partial f_{01}}{\partial p_{1x}} \qquad (13.53)$$

(the x-axis has been chosen in the direction of the electric field). If we retain these relations, although they are not quite accurate, we shall find that two more terms in Eq. (13.52) cancel each other, and we obtain the equation

$$e\mathbf{E} \frac{\partial \Delta f_1}{\partial p_{1x}} = \left(\frac{\partial f_{01}}{\partial t}\right)_{col} \qquad (13.54)$$

or, if we use (13.53) and the integral representation for the collision term,

$$e E \, \frac{\partial}{\partial p_{1x}} \left(\tau e E \, \frac{\partial f_{01}}{\partial p_{1x}}\right) = \int (f_{01} f_2 - f'_{01} f'_2) |\mathbf{v}_1 - \mathbf{v}_2| \, ds_0 \, d\Omega_2 \qquad (13.55)$$

The left-hand side of this equation is not isotropic, i.e. it also includes a correction to the non-isotropic part of the distribution function Δf_1. We shall disregard this correction, and to obtain an equation determining the isotropic function f_{01}, we shall average the right-hand and left-hand sides over all possible directions of the momentum $\mathbf{p}_1$. For this end, both sides of the equation must be multiplied by $d\Omega_1$. The result must be integrated in the momentum space of an electron over the spherical layer for which the magnitude of the momentum is larger than p_1, but less than $p_1 + dp_1$, or, if we speak of the energy of an electron, over the layer for which the energy changes from ε_1 to $\varepsilon_1 + d\varepsilon_1$. Integration over such a layer is equivalent to averaging over the angles characterizing the direction of the momentum and multiplication by (see Sec. 3.7)

$$d\Omega_1 = 4\pi p_1^2 \, dp_1 = 4 \sqrt{2} \, \pi m_2^{3/2} \sqrt{\varepsilon_1} \, d\varepsilon_1 = g\,(\varepsilon_1) \, d\varepsilon_1 \qquad (13.56)$$

The right-hand side of (13.55) is isotropic, and is therefore simply multiplied by $g\,(\varepsilon_1) \, d\varepsilon_1$. To transform the left-hand side, we must go over from derivatives with respect to p_{1x}

to derivatives with respect to the energy. Hence,

$$J = eE \frac{\partial}{\partial p_{1x}} \left(\tau eE \frac{\partial f_{01}}{\partial p_{1x}} \right) = e^2 E'^2 \frac{\partial}{\partial p_{1x}} \left(\tau \frac{\partial f_{01}}{\partial \varepsilon_1} \frac{\partial \varepsilon_1}{\partial p_{1x}} \right)$$

Since

$$\frac{\partial \varepsilon_1}{\partial p_{1x}} = \frac{1}{2m_1} \frac{\partial}{\partial p_{1x}} (p_{1x}^2 + p_{1y}^2 + p_{1z}^2) = \frac{p_{1x}}{m_1}$$

we further obtain

$$J = e^2 E^2 \frac{\partial}{\partial p_{1x}} \left(\tau \frac{\partial f_{01}}{\partial \varepsilon_1} \frac{p_{1x}}{m_1} \right)$$

$$= \frac{e^2 E^2}{m_1} \left[\tau \frac{\partial f_{01}}{\partial \varepsilon_1} + p_{1x} \frac{\partial}{\partial p_{1x}} \left(\tau \frac{\partial f_{01}}{\partial \varepsilon_1} \right) \right]$$

We again pass over to the derivative with respect to the energy

$$\frac{\partial}{\partial p_{1x}} \left(\tau \frac{\partial f_{01}}{\partial \varepsilon_1} \right) = \frac{\partial}{\partial \varepsilon_1} \left(\tau \frac{\partial f_{01}}{\partial \varepsilon_1} \right) \frac{\partial \varepsilon}{\partial p_{1x}} = \frac{\partial}{\partial \varepsilon_1} \left(\tau \frac{\partial f_{01}}{\partial \varepsilon_1} \right) \frac{p_{1x}}{m_1}$$

and finally obtain the following expression for the left-hand side:

$$J = \frac{e^2 E^2}{m_1} \left[\tau \frac{\partial f_{01}}{\partial \varepsilon_1} + \frac{p_{1x}^2}{m_1} \frac{\partial}{\partial \varepsilon_1} \left(\tau \frac{\partial f_{01}}{\partial \varepsilon_1} \right) \right]$$

Averaging of it over the angles with a view to the fact that $\langle p_{1x}^2 \rangle / (2m_1) = \varepsilon_1/3$ yields

$$I = \frac{e^2 E^2}{m_1} \left[\tau \frac{\partial f_{01}}{\partial \varepsilon_1} + \frac{2}{3} \varepsilon_1 \frac{\partial}{\partial \varepsilon_1} \left(\tau \frac{\partial f_{01}}{\partial \varepsilon_1} \right) \right]$$

$$= \frac{e^2 E^2}{m_1 \sqrt{\varepsilon_1}} \frac{2}{3} \frac{\partial}{\partial \varepsilon_1} \left(\varepsilon_1^{3/2} \tau \frac{\partial f_{01}}{\partial \varepsilon_1} \right)$$

Consequently, the left-hand side, when integrated over a spherical layer in momentum space, leads to

$$\frac{e^2 E^2}{m_1 \sqrt{\varepsilon_1}} \frac{2}{3} \frac{\partial}{\partial \varepsilon_1} \left(\varepsilon_1^{3/2} \tau \frac{\partial f_{01}}{\partial \varepsilon_1} \right) g(\varepsilon_1) \, d\varepsilon_1$$

Hence, the equation for the isotropic part of the distribution function becomes

$$\frac{e^2 E^2}{m_1 \sqrt{\varepsilon_1}} \frac{2}{3} \frac{\partial}{\partial \varepsilon_1} \left(\varepsilon_1^{3/2} \tau \frac{\partial f_{01}}{\partial \varepsilon_1} \right) g(\varepsilon_1) \, d\varepsilon_1$$

$$= \int (f_{01} f_2 - f'_{01} f'_2) |\mathbf{v}_1 - \mathbf{v}_2| \, ds_0 \, d\Omega_2 g(\varepsilon_1) \, d\varepsilon_1 \quad (13.57)$$

The right-hand side of this equation determines the number of electrons leaving the spherical layer $d\varepsilon_1$ owing to collisions with molecules. In other words, it determines the effect of energy transfer from electrons to molecules. The left-hand side depends on the field and shows that under the action of the field, the non-isotropic part of the distribution function, which itself is proportional to the electric field, changes slightly and gives an addition to the isotropic part, i.e. describes the effect of heating of the electron gas. The further transformations are aimed at representing the right-hand side of this integral equation in a simpler form. It is found that by using the condition of smallness of the energy transmitted by the electrons when colliding with the molecules, we can reduce this equation to a relatively simple differential equation.

To reduce calculations, it is good to integrate both sides of (13.57) from $\varepsilon_1 = 0$ to ε_1, thus having to do not with a change in the number of particles whose energy is confined within the interval $d\varepsilon_1$, but with a change in the number of particles having an energy less than ε_1. The left-hand side determining the change due to heating in the electric field is

$$\int_0^{\varepsilon_1} \frac{e^2 E^2}{m_1 \sqrt{\varepsilon_1}} \frac{2}{3} \frac{\partial}{\partial \varepsilon_1} \left(\varepsilon_1^{3/2} \tau \frac{\partial f_{01}}{\partial \varepsilon_1} \right) g(\varepsilon_1) \, d\varepsilon_1$$

$$= 4 \sqrt{2} \, \pi m_1^{1/2} \frac{2}{3} \varepsilon_1^{3/2} \tau \frac{\partial f_{01}}{\partial \varepsilon_1} e^2 E^2 \qquad (13.58)$$

where the representation of $g(\varepsilon_1) \, d\varepsilon_1$ according to (13.56) has been used. The right-hand side taking into account the change due to collisions is written as follows:

$$\int_0^{\varepsilon_1} \int (f_{01} f_2 - f_{01}' f_2') |\mathbf{v}_1 - \mathbf{v}_2| \, ds_0 \, d\Omega_2 g(\varepsilon_1) \, d\varepsilon_1$$

$$= \int_0^{\varepsilon_1} \int f_{01} f_2 |\mathbf{v}_1 - \mathbf{v}_2| \, ds_0 \, d\Omega_2 g(\varepsilon_1) \, d\varepsilon_1$$

$$- \int_0^{\varepsilon_1} \int f_{01}' f_2' |\mathbf{v}_1 - \mathbf{v}_2| \, ds_0 \, d\Omega_2 g(\varepsilon_1) \, d\varepsilon_1 \qquad (13.59)$$

Let the forward transition consist in that particles having the momenta $\mathbf{p}_1$ and $\mathbf{p}_2$ obtain the momenta $\mathbf{p}_1'$ and $\mathbf{p}_2'$ after

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a collision, the initial energy ε_1 of an electron changing to $\varepsilon_1 - \delta\varepsilon_1$. If in the second integral on the right-hand side of (13.59) we pass over to primed variables, i.e. to momenta after a collision, it acquires the form:

$$\int_0^{\varepsilon_1} \int f_{01}' f_2' |\mathbf{v}_1 - \mathbf{v}_2| ds_0 \, d\Omega_2 g(\varepsilon_1) \, d\varepsilon_1$$

$$= \int_0^{\varepsilon_1 - \delta\varepsilon_1} f_{01}' f_2' |\mathbf{v}_1' - \mathbf{v}_2'| ds_0' \, d\Omega_2' g(\varepsilon_1') \, d\varepsilon_1'$$

where $(\varepsilon_1 - \delta\varepsilon_1)$ is the energy of an electron after a collision corresponding to the value which it obtains at the new values of the variables. The last expression differs from the first term on the right-hand side of (13.59) only in the designation of the integration variables and in the value of the upper limit. The designation of the integration variables is of no significance and cannot change the value of the integral itself. In this connection, we can write

$$\int_0^{\varepsilon_1} \left(\frac{\partial f_{01}}{\partial t} \right)_{\text{col}} g(\varepsilon) \, d\varepsilon = \int_0^{\varepsilon_1} - \int_0^{\varepsilon_1 - \delta\varepsilon_1}$$

$$= \int_{\varepsilon_1 - \delta\varepsilon_1}^{\varepsilon_1} \int f_{01} f_2 |\mathbf{v}_1 - \mathbf{v}_2| ds_0 \, d\Omega_2 g(\varepsilon_1) \, d\varepsilon_1 \qquad (13.60)$$

To continue our calculations, we must consider in greater detail the quantity $\delta\varepsilon_1$ characterizing the change in the energy of an electron in the course of a collision:

$$\delta\varepsilon_1 = \frac{m_1 v_1^2}{2} - \frac{m_1 v_1'^2}{2} \qquad (13.61)$$

With the help of relations (13.15) and (13.16), it is a simple matter to obtain

$$v_1^2 = v_s^2 + \frac{m_2^2}{(m_1 + m_2)^2} v_r^2 + \frac{2m_2}{m_1 + m_2} \mathbf{v}_s \mathbf{v}_r$$

$$v_1'^2 = v_s^2 + \frac{m_2^2}{(m_1 + m_2)^2} v_r^2 + \frac{2m_2}{m_1 + m_2} \mathbf{v}_s \mathbf{v}_r'$$

so that after introducing these expressions into (13.61), we find

$$\delta\varepsilon_1 = \frac{m_1 m_2}{m_1 + m_2} \mathbf{v}_s (\mathbf{v}_r - \mathbf{v}_r') \qquad (13.62)$$

Expressing the velocity of the centre of mass of the system and the relative velocities in terms of the absolute ones, we arrive at the following expression that is convenient for our further analysis:

$$\delta\varepsilon_1 = \frac{m_1 m_2}{m_1 + m_2} \frac{m_1 \mathbf{v}_1 + m_2 \mathbf{v}_2}{m_1 + m_2} \frac{m_1 + m_2}{m_2} (\mathbf{v}_1 - \mathbf{v}_s - \mathbf{v}_1' + \mathbf{v}_s)$$

$$= \frac{m_1 m_2}{m_1 + m_2} \mathbf{v}_2 (\mathbf{v}_1 - \mathbf{v}_1') + \frac{m_1^2}{m_1 + m_2} \mathbf{v}_1 (\mathbf{v}_1 - \mathbf{v}_1') \qquad (13.63)$$

The velocity of an electron v_1 is $\sqrt{m_2/m_1}$ times larger than the velocity v_2 of a molecule, therefore the first term has the order

$$\frac{m_1 m_2}{m_1 + m_2} \mathbf{v}_2 (\mathbf{v}_1 - \mathbf{v}_1') \approx m_1 \mathbf{v}_2 \mathbf{v}_1 \approx m_1 \sqrt{\frac{m_1}{m_2}} v_1^2$$

i.e. it is $\sqrt{m_2/m_1}$ times larger than the second term having the order $(m_1/m_2) m_1 v_1^2$. In estimating the value of the first term, however, it must be taken into account that the velocity $\mathbf{v}_2$ may have any direction relative to $\mathbf{v}_1$. Although the molecule's velocity does affect somewhat the direction of the electron's velocity $\mathbf{v}_1'$ after a collision, this influence is small; the direction of the velocity after a collision depends mainly on the impact parameter and remains almost the same as in scattering by a fixed molecule. With the direction of $\mathbf{v}_2$ being arbitrary, this signifies that after averaging, the first term vanishes. The mean value of $\delta\varepsilon_1$ is thus determined by the second term and can be represented by the following expression:

$$\delta\varepsilon_1 = \frac{m_1^2}{m_1 + m_2} \mathbf{v}_1 (\mathbf{v}_1 - \mathbf{v}_1') \approx \frac{m_1^2}{m_2} (v_1^2 - \mathbf{v}_1 \mathbf{v}_1')$$

$$\approx \frac{m_1^2 v_1^2}{m_2} (1 - \cos\theta) = 2 \frac{m_1}{m_2} \varepsilon_1 (1 - \cos\theta) \qquad (13.64)$$

where ε_1 is the energy of an electron before a collision, and θ is an angle close to the scattering angle because the velocities $\mathbf{v}_1$ and $\mathbf{v}_1'$ are close to $\mathbf{v}_r$ and $\mathbf{v}_r'$.

Let us now consider the square of $\delta\varepsilon_1$:

$$\delta\varepsilon_1^2 = \left(\frac{m_1 m_2}{m_1 + m_2}\right)^2 [\mathbf{v}_2 (\mathbf{v}_1 - \mathbf{v}_1')]^2$$

$$+ 2 \frac{m_1 m_2}{m_1 + m_2} \mathbf{v}_2 (\mathbf{v}_1 - \mathbf{v}_1') \frac{2m_1}{m_2} \varepsilon_1 (1 - \cos\theta) + 4 \frac{m_1^2}{m_2^2} \varepsilon_1^2 (1 - \cos\theta)^2$$

$$(13.65)$$

The middle term vanishes upon averaging owing to the directions of $\mathbf{v}_2$ being arbitrary, and it may be disregarded. The last term is m_1/m_2 times smaller than (13.64) because it equals the square of this small quantity. The first term is of the same order with respect to m_1/m_2 as (13.64). Indeed,

$$\left(\frac{m_1 m_2}{m_1 + m_2}\right)^2 [\mathbf{v}_2 (\mathbf{v}_1 - \mathbf{v}_1')]^2 \approx m_1^2 v_{2\xi}^2 (\mathbf{v}_1 - \mathbf{v}_1')^2$$

where $v_{2\xi}$ is the projection of $\mathbf{v}$ onto the direction of $\mathbf{v}_1 -$ $- \mathbf{v}_1'$. The mean square projection of a molecule's velocity in accordance with the Maxwell distribution is

$$\langle v_{2\xi}^2 \rangle = \frac{kT}{m_2}$$

Further,

$$(\mathbf{v}_1 - \mathbf{v}_1')^2 = v_1^2 + v_1'^2 - 2\mathbf{v}_1\mathbf{v}_1' = 2v_1^2 - 2\mathbf{v}_1\mathbf{v}_1' = 2v_1^2 (1 - \cos\theta)$$

Therefore, the mean value of the first term in (13.65) is

$$\frac{m_1^2}{m_2} kT 2v_1^2 (1 - \cos\theta) = 4\frac{m_1}{m_2} kT\varepsilon_1 (1 - \cos\theta)$$

i.e. it is of the same order with respect to the small quantity m_1/m_2 as (13.64) is. Hence,

$$\langle \delta\varepsilon_1^2 \rangle = 4\frac{m_1}{m_2} kT\varepsilon_1 (1 - \cos\theta) \qquad (13.66)$$

and, consequently, the mean values of $\delta\varepsilon_1$ and $\delta\varepsilon_1^2$ with respect to the directions of the molecule's velocities are quantities of the same order relative to the parameter m_1/m_2. This is very important for our further approximate calculations because it points to the necessity of simultaneously taking the terms $\delta\varepsilon_1$ and $\delta\varepsilon_1^2$ into account.

Let us now return to Eq. (13.57). A glance at (13.63) shows that $\delta\varepsilon_1$ depends on $\mathbf{v}_1$ and on the scattering angle because the latter determines the velocity $\mathbf{v}_1'$. In this connection, it is good practice to first integrate over ε_1, and then over the remaining variables:

$$\int_0^{\varepsilon_1} \left(\frac{\partial f_{01}}{\partial t}\right)_{\text{col}} g(\varepsilon_1') \, d\varepsilon_1'$$

$$= \int f_2 \, d\Omega_2 \int_{\varepsilon_1 - \delta\varepsilon_1}^{\varepsilon_1} ds_0 \, f_{01}(\varepsilon_1') |\mathbf{v}_1 - \mathbf{v}_2| g(\varepsilon_1') \, d\varepsilon_1' \qquad (13.67)$$

The integral

$$\int\limits_{\varepsilon_1-\delta\varepsilon_1}^{\varepsilon_1} ds_0\, f_{01}\,(\varepsilon_1')\,|\,\mathbf{v}_1-\mathbf{v}_2|\,g\,(\varepsilon_1')\,d\varepsilon_1' \qquad (13.68)$$

can be evaluated approximately, taking advantage of the circumstance that the integration interval $\delta\varepsilon_1$ is small in comparison with the mean energy of an electron ε_1 (it is m_1/m_2 times smaller). We shall also disregard $\mathbf{v}_2$ in $|\,\mathbf{v}_1 - \mathbf{v}_2\,|$. The electron distribution function $f_{01}\,(\varepsilon_1')$ should be expanded in the deviation of the energy from ε_1, and only the first two terms taken:

$$f_{01}\,(\varepsilon_1') = f_{01}\,(\varepsilon_1) + (\varepsilon_1' - \varepsilon_1)\,\frac{\partial f_{01}}{\partial \varepsilon_1} \qquad (13.69)$$

Indeed, the following terms of the expansion after integration with respect to ε_1' give quantities of the order of $\delta\varepsilon_1^3$ and higher that may be ignored in comparison with the terms proportional to $\delta\varepsilon_1$ and $\delta\varepsilon_1^2$.

Substitution of (13.69) into (13.68) yields

$$\int\limits_{\varepsilon_1-\delta\varepsilon_1}^{\varepsilon_1} ds_0\, f_{01}\,(\varepsilon_1)\, v_1 g\,(\varepsilon_1')\,d\varepsilon_1' + \int\limits_{\varepsilon_1-\delta\varepsilon_1}^{\varepsilon_1} ds_0\, \frac{df_{01}}{d\varepsilon_1}\,(\varepsilon_1'-\varepsilon_1)\, v_1 g\,(\varepsilon_1')\,d\varepsilon_1'$$

$$= ds_0 f_{01}\,(\varepsilon_1)\, v_1 g\,(\varepsilon_1)\,\delta\varepsilon_1 - ds_0\,\frac{df_{01}}{d\varepsilon_1}\, v_1 g\,(\varepsilon_1)\,\frac{\delta\varepsilon_1^2}{2}$$

where a certain mean value of the quantity $ds_0 v_1 g\,(\varepsilon_1')$ is taken for the interval $\delta\varepsilon_1$. Since the integration interval $\delta\varepsilon_1$ is small in comparison with the mean energy, this application of the mean-value theorem in transformation of the integral affects the final result only slightly. Now the initial integral (13.60) acquires the following form

$$\int\limits_0^{\varepsilon_1} \left(\frac{\partial f_{01}}{\partial t} \right)_{col} g\,(\varepsilon_1')\,d\varepsilon_1' = f_{01}\,(\varepsilon_1)\, g\,(\varepsilon_1)\, v_1 \int \delta\varepsilon_1\, ds_0 f_2\, d\Omega_2$$

$$- \frac{df_{01}}{d\varepsilon_1}\,\frac{1}{2}\, g\,(\varepsilon_1)\, v_1 \int \delta\varepsilon_1^2\, ds_0 f_2\, d\Omega_2 \qquad (13.70)$$

Integration over $d\Omega_2$ corresponds to averaging over all the directions of $\mathbf{v}_2$ and evaluation of the mean values of the function of v_2 multiplied, in addition, by the number

of molecules. Hence,

$$\int \delta\varepsilon_1\,ds_0 f_2\,d\Omega_2 = 2\,\frac{m_1}{m_2}\,n_2\varepsilon_1\,\int (1-\cos\theta)\,ds_0 = \frac{2m_1}{m_2}\,n_2\,\langle s_0\rangle\,\varepsilon_1$$

and

$$\int \delta\varepsilon_1^2\,ds_0 f_2\,d\Omega_2 = 4\,\frac{m_1}{m_2}\,kT\varepsilon_1\,\int (1-\cos\theta)\,ds_0 = \frac{4m_1}{m_2}\,n_2\,\langle s_0\rangle\,kT\varepsilon_1$$

Here we used equations (13.64) and (13.66), and also the definition (13.14) of the effective scattering cross section. The symbol $\langle s_0\rangle$ stands for the mean scattering cross section for the interval $\delta\varepsilon_1$. It does not virtually differ from s_0. This completes the evaluation of the integral (13.67).

Equating the evaluated integral to expression (13.58), we obtain an equation for the function f_{01}:

$$4\,\sqrt{2}\,\pi m_1^{1/2}\,\frac{2}{3}\,\varepsilon_1^{3/2}\tau\,\frac{df_{01}}{d\varepsilon_1}\,e^2 E^2$$
$$= 4\,\sqrt{2}\,\pi m_1^{3/2}\varepsilon_1^{1/2} n_2\,\langle s_0\rangle\,v_1\varepsilon_1\,\frac{2m_1}{m_2}\left(f_{01} - kT\,\frac{df_{01}}{d\varepsilon_1}\right)$$

After cancelling the common factors and taking into account that $n_2\,\langle s_0\rangle\,v_1 = 1/\tau$ we obtain the differential equation

$$f_{01} = \left(kT + \frac{m_2}{3m_1^2}\,\tau^2 e^2 E^2\right)\frac{df_{01}}{d\varepsilon_1} \qquad (13.71)$$

that is solved quite simply by the method of separating the variables. It is not difficult to see by direct substitution that the required distribution function has the form

$$f_{01} = C\,\exp\left[\,-\int_0^{\varepsilon_1}\frac{d\varepsilon_1'}{kT + (m_2/m_1^2)/(\tau^2 e^2 E^2/3)}\right] \qquad (13.72)$$

The constant C, as always, is determined by the normalization condition

$$\int_0^\infty f_{01}g\,(\varepsilon_1)\,d\varepsilon_1 = n_1$$

where n_1 is the electron concentration.

Consequently, *when account is taken of heating of electrons by a constant electric field, the velocity distribution function*

of the electrons has the form

$$f_1 = f_{01} + \Delta f_1$$

where f_{01} is the isotropic part of the distribution function determined by expression (13.72), *and Δf_1 is a correction to it that can be taken in the form of* (13.53), *the isotropic function* (13.72) *being introduced as f_{01}*

If

$$\frac{m_2}{m_1^2}\frac{\tau^2 e^2 E^2}{3} = \frac{m_2}{m_1}\frac{\lambda^2 e^2 E^2}{6\varepsilon_1} \ll kT \qquad (13.73)$$

from (13.72) we obtain the Maxwell distribution function

$$f_{01} = C\exp\left(-\int_0^\varepsilon \frac{d\varepsilon}{kT}\right) = C\exp\left(-\frac{\varepsilon}{kT}\right)$$

Since in this case the mean energy of the electrons is $\frac{3}{2}kT$, it follows from (13.73) that heating of the electron gas begins at electric fields satisfying the condition

$$\frac{m_2}{m_1}\frac{\lambda^2 e^2 E^2}{9kT} \approx kT$$

or

$$\lambda e E\sqrt{\frac{m_2}{m_1}} \approx 3kT \qquad (13.74)$$

In gases, where the free path may be large, and where owing to the relatively low conductance the electric field strength is also large, the condition of heating is observed quite readily. In metals, the conductance is very high, and it is virtually impossible to reach an electric field strength at which the mean energy of the electrons depends appreciably on the field. In semiconductors in the proper conditions, heating of the electrons is possible.

If the electric field is very strong so that an inequality that is the opposite of (13.73) is observed, by disregarding the term kT we can obtain

$$f_{01} = C\exp\left[-\int_0^\varepsilon \frac{d\varepsilon_1}{(m_2/m_1)\,(\lambda^2 e^2 E^2/6\varepsilon_1)}\right]$$

The form of the distribution function depends on how the free path changes with the energy. For instance, in scatter-

ing by neutral molecules, when we may consider that the free path does not depend on the energy we obtain the **Druyvesteyn distribution**

$$f_{01} = C \exp \left[-\frac{3\varepsilon_1^2}{(m_2/m_1)\,\lambda^2 e^2 E^2} \right]$$

that greatly differs from the Maxwellian distribution. Another example is given in the exercises to the present chapter.

Here we shall terminate our treatment of the non-equilibrium distribution functions, although the considered example far from exhausts all the cases encountered in practice. The behaviour of electrons in a high-frequency electric field, the influence of a magnetic field, and the part played by inelastic collisions are examples of the problems being worked out for a number of years and are continuing to be worked on at present. Their consideration, however, is beyond the scope of this book.

Exercises

1. *Show that the Fermi-Dirac distribution follows from the detailed balancing principle and the form of the collision term* (13.28) *taking into account the Pauli exclusion principle.*
Solution. It follows from the detailed balancing principle that in equilibrium, the integrand in (13.28) must vanish. Hence

$$f_1 \left[1 - (2\pi\hbar)^3 f_1' \right] f_2 = f_1' \left[1 - (2\pi\hbar)^3 f_1 \right] f_2'$$

or

$$\frac{f_1}{1 - (2\pi\hbar)^3 f_1}\, f_2 = \frac{f_1'}{1 - (2\pi\hbar)^3 f_1'}\, f_2'$$

Here f_2 is the Maxwell distribution function, i.e.

$$f_2 = \frac{1}{(2\pi\hbar)^3} \exp \left(\frac{\mu - \varepsilon_2}{kT} \right)$$

If

$$\frac{(2\pi\hbar)^3 f_1}{1 - (2\pi\hbar)^3 f_1} = \exp \left(\frac{\mu - \varepsilon_1}{kT} \right)$$

where ε_1 is the energy of an electron before a collision, then detailed balancing is observed provided that

$$\varepsilon_1 + \varepsilon_2 = \varepsilon_1' + \varepsilon_2'$$

Finding f_1 from the preceding equation, we obtain

$$f_1 = \frac{1}{(2\pi\hbar)^3}\, \frac{1}{\exp\left[(\varepsilon_1 - \mu)/(kT)\right] + 1}$$

Q.E.D.

2. *At what energy dependence of the relaxation time does the non-equilibrium distribution function f_{01} remain Maxwellian? What is the effective temperature of this distribution?*

Solution. Examination of (13.72) shows that at $\tau = $ const we obtain a Maxwellian distribution with the effective temperature

$$T_{\text{eff}} = T + \frac{m_2 \tau^2 e^2 E^2}{3m_1^2 k}$$

Chapter 14

FLUCTUATIONS

14.1. Significance of Fluctuations

The characteristics dealt with in statistical physics such as, for example, the internal energy or the pressure, are obtained as a result of averaging the relevant mechanical quantities relating to the system of particles being studied. Since the number of particles in a system is usually very large, the experimentally measured values are close to their mathematical expectations (mean values). Nevertheless, chaotic deviations from the mean values known as **fluctuations** sometimes become significant. The magnitude of fluctuations is generally characterized by the dispersion, i.e. the mean-square value of the deviation of a random variable from its mathematical expectation. For instance, if we are considering the energy of a system of particles, its fluctuation is characterized by the quantity

$$\langle \Delta \mathscr{E}^2 \rangle = \langle (\mathscr{E} - U)^2 \rangle$$

where U is the internal energy, i.e. the mathematical expectation of the energy of a system. Examples of fluctuations were given on earlier pages. For instance, in Sec. 3.1, we investigated the random deviations of the number of particles in a volume from their mean number, and in Sec. 5.6—the random fluctuations of the pointer of a spring balance, and also of the voltage across a capacitor connected in an oscillatory circuit.

Generally, and this was noted in Secs. 3.1 and 5.6, the fluctuations are small so that they may be ignored. There is a very important branch of physics and engineering, however, in which they play a defining role. We have in view

accurate measurements and communication equipment. The improvement in the sensitivity of measuring instruments and receiving devices resulted in the fact that in many cases the maximum possibilities are realized, which are determined by the fluctuations. Let us explain what has been said by a specific example.

To measure the radiated power in the visible and infrared regions of the spectrum, thermal receivers of radiation are sometimes used. The principle of their operation consists in that the radiation to be measured is directed onto a small blackened area where it is absorbed, thus heating the area. The elevation of the temperature, proportional to the magnitude of the incident power, is measured with the aid of a sensitive thermocouple connected to the area, or in some other way. The limiting sensitivity of such receivers is determined by the fluctuations of the output voltage of the instrument because a received signal whose magnitude is smaller than that of the fluctuations cannot be detected against the background of the chaotic bursts of the output voltage.

Different causes of the voltage fluctuations or, as is otherwise said, of the **noise**, can be indicated. First of all, if a thermocouple is being used to measure overheating, it has a definite resistance, and in the electric circuit of the thermocouple with the measuring instrument there appears a random signal due to the thermal motion of the electrons and to the fluctuation of their number. This noise will be treated in 14.5. In addition to the electric noise, it must be taken into account that the receiving area, which to increase the sensitivity of the device is made very small and light, continuously exchanges energy with its surroundings. The result is random fluctuations of the area's temperature that the thermocouple transforms into a random electrical signal. Temperature fluctuations together with those of many other thermodynamic quantities will be treated in Secs. 14.3 and 14.4. Finally, it must be taken into account that the radiation being registered is incident on the receiving area together with a background due to the emission by radiating objects in the field of vision of the receiver. The background produces radiation whose power continuously fluctuates, and in this way contributes to the noise voltage.

Fluctuations may be conditionally divided into those occurring in equilibrium systems and those that manifest themselves upon deviations of a system from equilibrium. The main role is played by the former, as a rule, because the deviations from equilibrium with which we usually have to do are small. In studying fluctuations in equilibrium systems, we may use the Gibbs distribution, and this allows us to present a complete theory of the phenomenon. An example of the fluctuations manifesting themselves in a non-equilibrium system is the shot noise appearing in the flow of an electric current. They will be treated in Sec. 14.5.

14.2. Fluctuations of the Number of Particles and Volume

Let us apply the Gibbs distribution to calculating the fluctuation of the number of particles in a definite volume. We shall obtain a general relation from which, in particular for a classical ideal gas, we obtain the result given in Sec. 3.1, but which, on the other hand, also holds for other systems (for example, for a gas consisting of bosons or fermions).

In Sec. 8.5, we obtained the condition (8.33) determining the mean number of particles in a system by differentiation of the normalization condition for the Gibbs grand canonical distribution with respect to μ. This condition can be written in the form

$$\sum_{\nu N} \left(\frac{\partial \Omega^*}{\partial \mu} + N \right) \exp\left(\frac{\Omega^* - \mathscr{E}_{\nu N} + \mu N}{kT} \right) = 0 \qquad (14.1)$$

To obtain the mathematical expectation of the square of the number of particles, we differentiate it with respect to the same parameter again. The result is

$$\sum_{\nu N} \left[\frac{\partial^2 \Omega^*}{\partial \mu^2} + \frac{1}{kT} \left(\frac{\partial \Omega^*}{\partial \mu} + N \right)^2 \right] \exp\left(\frac{\Omega^* - \mathscr{E}_{\nu N} + \mu N}{kT} \right) = 0 \tag{14.2}$$

Opening the internal parentheses, we find

$$\sum_{\nu N} \left[\frac{\partial^2 \Omega^*}{\partial \mu^2} + \frac{1}{kT} \left(\frac{\partial \Omega^*}{\partial \mu} \right)^2 + \frac{2}{kT} \frac{\partial \Omega^*}{\partial \mu} N + \frac{1}{kT} N^2 \right]$$
$$\times \exp\left(\frac{\Omega^* - \mathscr{E}_{\nu N} + \mu N}{kT} \right) = 0$$

or

$$\frac{\partial^2 \Omega^*}{\partial \mu^2} \sum_{\nu N} \exp\left(\frac{\Omega^* - \mathscr{E}_{\nu N} + \mu N}{kT}\right)$$

$$+ \frac{1}{kT}\left(\frac{\partial \Omega^*}{\partial \mu}\right)^2 \sum_{\nu N} \exp\left(\frac{\Omega^* - \mathscr{E}_{\nu N} + \mu N}{kT}\right)$$

$$+ \frac{2}{kT}\frac{\partial \Omega^*}{\partial \mu} \sum_{\nu N} N \exp\left(\frac{\Omega^* - \mathscr{E}_{\nu N} - \mu N}{kT}\right)$$

$$+ \frac{1}{kT} \sum_{\nu N} N^2 \exp\left(\frac{\Omega^* - \mathscr{E}_{\nu N} + \mu N}{kT}\right) = 0 \qquad (14.3)$$

Use of the normalization condition and of the condition for determining the mean values given below:

$$\sum_{\nu N} \exp\left(\frac{\Omega^* - \mathscr{E}_{\nu N} + \mu N}{kT}\right) = 1$$

$$\sum_{\nu N} N \exp\left(\frac{\Omega^* - \mathscr{E}_{\nu N} + \mu N}{kT}\right) = \langle N \rangle$$

$$\sum_{\nu N} N^2 \exp\left(\frac{\Omega^* - \mathscr{E}_{\nu N} + \mu N}{kT}\right) = \langle N^2 \rangle$$

allows us to write (14.3) as follows:

$$\frac{\partial^2 \Omega^*}{\partial \mu^2} + \frac{1}{kT}\left(\frac{\partial \Omega^*}{\partial \mu}\right)^2 + \frac{2}{kT}\frac{\partial \Omega^*}{\partial \mu}\langle N \rangle + \frac{1}{kT}\langle N^2 \rangle = 0$$

Since

$$\frac{\partial \Omega^*}{\partial \mu} = -\langle N \rangle \qquad (14.4)$$

the result obtained reduces to

$$\frac{\partial^2 \Omega^*}{\partial \mu^2} + \frac{1}{kT}[\langle N \rangle^2 - 2\langle N \rangle^2 + \langle N^2 \rangle] = 0$$

or after collecting terms and multiplying by kT

$$kT\frac{\partial^2 \Omega^*}{\partial \mu^2} + (\langle N^2 \rangle - \langle N \rangle^2) = 0$$

Since a dispersion by definition equals $\langle \Delta N^2 \rangle = \langle N^2 \rangle - \langle N \rangle^2$, we have

$$\langle \Delta N^2 \rangle = -kT\frac{\partial^2 \Omega^*}{\partial \mu^2} \qquad (14.5)$$

or, with a view to (14.4)

$$\langle \Delta N^2 \rangle = kT \, \frac{\partial \langle N \rangle}{\partial \mu} \tag{14.6}$$

Hence, *from the Gibbs distribution for the magnitude of the fluctuations of the mean number of particles, we obtain formulas* (14.5) *and* (14.6). *Introducing into* (14.5) *the relevant expression for the omega-potential, we can find the dispersion of the number of particles in a system.*

For a classical ideal gas, by (10.16) and (10.18), we have

$$\Omega^* = -\frac{4\pi \, (kT)^{5/2}}{(2\pi\hbar)^3} \, (2m_0)^{3/2} \, V e^{\mu/(kT)}$$

that is

$$\langle N \rangle = -\frac{\partial \Omega^*}{\partial \mu} = \frac{4\pi \, (kT)^{3/2}}{(2\pi\hbar)^3} \, (2m_0)^{3/2} V e^{\mu/(kT)}$$

and

$$\langle \Delta N^2 \rangle = kT \, \frac{\partial \langle N \rangle}{\partial \mu} = \langle N \rangle \tag{14.7}$$

This result was obtained in a more direct way in Sec. 3.1. Inspection of (14.7) shows that the relative magnitude of a fluctuation, i.e. the ratio of the square root of the dispersion to the mean number of particles, is

$$\frac{\sqrt{\langle \Delta N^2 \rangle}}{\langle N \rangle} = \frac{1}{\sqrt{\langle N \rangle}}$$

Since the number of particles with which we have to do in real systems is extraordinarily large, the fluctuations, as a rule, are unnoticeable, and it is quite sufficient to know only the mean number of particles. With very accurate measurements in small systems, however, the fluctuations disclose themselves and limit the accuracy of measurements to a certain extent.

Let us consider a boson gas and determine the dispersion of the number of particles in a given state *i*. By (9.5), we have

$$\Omega_i^* = kT \ln \left[1 - \exp \left(\frac{\mu - \varepsilon_i}{kT} \right) \right] \tag{14.8}$$

We further have

$$\langle n_i \rangle = -\frac{\partial \Omega_i^*}{\partial \mu} = \frac{1}{\exp \left[(\varepsilon_i - \mu)/(kT) \right] - 1} \tag{14.9}$$

(the Bose-Einstein distribution). From the general formula (14.6) for a fluctuation, we obtain

$$\langle \Delta n_i^2 \rangle = kT \, \frac{\partial \langle n_i \rangle}{\partial T} = \frac{\exp\left[(\varepsilon_i - \mu)/(kT)\right]}{\{\exp\left[(\varepsilon_i - \mu)/(kT)\right] - 1\}^2}$$

It is convenient to transform the last equation as follows:

$$\langle \Delta n_i^2 \rangle = \frac{\exp\left[(\varepsilon_i - \mu)/(kT)\right] - 1 + 1}{\{\exp\left[(\varepsilon_i - \mu)/(kT)\right] - 1\}^2}$$

$$= \frac{1}{\exp\left[(\varepsilon_i - \mu)/(kT)\right] - 1} + \frac{1}{\{\exp\left[(\varepsilon_i - \mu)/(kT)\right] - 1\}^2}$$

$$= \langle n_i \rangle + \langle n_i \rangle^2 \qquad (14.10)$$

where we have used expression (14.9). This formula differs from the classical one, but at large negative values of μ when the mean number of particles in a given state $\langle n_i \rangle$ is very small, we may disregard $\langle n_i \rangle^2$ in comparison with $\langle n_i \rangle$ and we thus obtain the classical result.

The dispersion of the total number of particles in a system can be obtained in an absolutely similar way proceeding from expression (9.6) for the omega-potential

$$\Omega^* = kT \sum_i \ln\left[1 + \exp\left(\frac{\mu - \varepsilon_i}{kT}\right)\right] \qquad (14.11)$$

Since the entire difference between (14.8) and (14.11) consists in that in the latter case summation is performed over all the states i, the final result naturally has the form

$$\langle \Delta N^2 \rangle = \sum_i \langle n_i \rangle \, (1 + \langle n_i \rangle) \qquad (14.12)$$

Hence, the dispersion of the total number of bosons equals the sum of the dispersions of the number of particles in each state i. This indicates the independence of the number of particles in different states.

After transition from the sum to an integral, expression (14.12) is written as

$$\langle \Delta N^2 \rangle = \int \langle n_i \rangle \, (1 + \langle n_i \rangle) \, g_\varepsilon \, d\varepsilon$$

$$= \int \frac{\exp\left[(\varepsilon - \mu)/(kT)\right]}{\{\exp\left[(\varepsilon - \mu)/(kT)\right] - 1\}^2} \, g_\varepsilon \, d\varepsilon \qquad (14.13)$$

where we have again used Eq. (14.10).

For photons, assuming that $\mu = 0$, $\varepsilon = \hbar\omega$, using (9.15), and taking into account two possible polarizations, we can write

$$\langle \Delta N^2 \rangle = 2 \int \frac{\exp[\hbar\omega/(kT)]}{\{\exp[\hbar\omega/(kT)] - 1\}^2} \frac{4\pi\omega^2\,d\omega}{(2\pi c)^3} V$$

If all the frequencies are registered, the lower integration limit is zero, the upper one is infinity, and therefore

$$\langle \Delta N^2 \rangle = \frac{8\pi(kT)^3}{(2\pi c)^3 \hbar^3} V \int_0^\infty \frac{e^x x^2\,dx}{(e^x - 1)^2} \tag{14.14}$$

where we have introduced the dimensionless integration variable $x = \hbar\omega/(kT)$. Since*

$$\int_0^\infty \frac{e^x x^2\,dx}{(e^x - 1)^2} = \frac{\pi^2}{3}$$

we finally obtain

$$\langle \Delta N^2 \rangle = \frac{1}{3}\left(\frac{kT}{\hbar c}\right)^3 V \tag{14.15}$$

In a similar way, we can calculate the dispersion for fermions. Using expressions (10.2) and (10.3), i.e.

$$\Omega_i^* = -kT \ln\left[1 + \exp\left(\frac{\mu - \varepsilon_i}{kT}\right)\right] \text{ and } \Omega^* = \sum_i \Omega_i^*$$

we shall arrive at the following relations:

$$\langle \Delta n_i^2 \rangle = \langle n_i \rangle (1 - \langle n_i \rangle) \tag{14.16}$$

$$\langle \Delta N^2 \rangle = \sum_i \langle n_i \rangle (1 - \langle n_i \rangle) \tag{14.17}$$

$$* \int_0^\infty \frac{x^2 e^x\,dx}{(e^x - 1)^2} = \int_0^\infty \frac{e^{-x} x^2\,dx}{(1 - e^{-x})^2} = \int_0^\infty x^2 e^{-x}(1 + 2e^{-x} + 3e^{-2x} + \ldots)\,dx$$

$$= \sum_{n=1}^\infty \int_0^\infty n x^2 e^{-nx}\,dx = 2\sum_{n=1}^\infty \frac{1}{n^2} = 2\frac{\pi^2}{6} = \frac{\pi^2}{3}$$

The value of the sum $\sum_{n=1}^\infty \frac{1}{n^2} = \frac{\pi^2}{6}$ is given, for example, in [19], p. 226.

Equation (14.17) after transition to an integral can be represented in the form

$$\langle \Delta N^2 \rangle = \int\limits_0^\infty \frac{\exp\left[(\varepsilon - \mu)/(kT)\right]}{\{\exp\left[(\varepsilon - \mu)/(kT)\right] - 1\}^2}\, g_\varepsilon\, d\varepsilon \qquad (14.18)$$

The fluctuations of the number of particles in a given volume are closely related to the question of the fluctuations of the volume with a given number of particles. Indeed, let us consider a specific example of a gas in a vessel (Fig. 14.1),
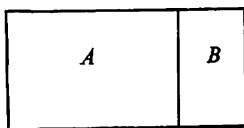
Fig. 14.1

which is a system with a given number of particles. Assume that a fluctuation has occurred as a result of which the entire gas has gathered in the part A of the vessel, so that no molecules remain in the part B. The same event can be interpreted in a different way. Assume that we are dealing with a system comprising the gas in the part A of the vessel. Now the fluctuation consists in that the number of particles in A increased by ΔN. It is evident that at not too small fluctuations, when the part B contains many particles, we have

$$\Delta N = \frac{\Delta V}{V}\, N \qquad (14.19)$$

where N is the total number of particles in the vessel, V is its volume, and ΔV is the volume of the part B. Squaring Eq. (14.19) and averaging it, we find

$$\langle \Delta V^2 \rangle = \langle \Delta N^2 \rangle \frac{1}{(N/V)^2} \qquad (14.20)$$

where the ratio N/V, equal also to the derivative $(\partial \langle N \rangle / \partial V)_T$, is the mean density of the particles. If we substitute for $\langle \Delta N^2 \rangle$ in (14.20) its value from (14.6), we obtain

$$\langle \Delta V^2 \rangle = kT\, \frac{\partial \langle N \rangle}{\partial \mu} \cdot \left(\frac{\partial \langle N \rangle}{\partial V} \right)_T^{-2} \qquad (14.21)$$

Further transformations are aimed at writing this expression in a simpler form.

At a constant temperature, the pressure is a function only of μ because the omega-potential is proportional to the volume, while the pressure is determined by the derivative $\partial\Omega^*/\partial V$. In this connection, we can write

$$\frac{\partial \langle N \rangle}{\partial \mu} = \left(\frac{\partial \langle N \rangle}{\partial P} \right)_T \left(\frac{\partial P}{\partial \mu} \right)_T$$

Since the following identity holds:

$$\frac{\partial P}{\partial \mu} = \frac{\partial}{\partial \mu} \left(-\frac{\partial \Omega^*}{\partial V} \right) = -\frac{\partial^2 \Omega^*}{\partial \mu\, \partial V} = \frac{\partial}{\partial V} \left(-\frac{\partial \Omega^*}{\partial \mu} \right) = \frac{\partial \langle N \rangle}{\partial V}$$

we can write (14.21) as

$$\langle \Delta V^2 \rangle = kT \left[\left(\frac{\partial \langle N \rangle}{\partial P} \right)_{T,\, V} \left(\frac{\partial \langle N \rangle}{\partial V} \right)_{T,\, \mu}^{-1} \right]$$

$$= kT \left[\left(\frac{\partial \langle N \rangle}{\partial P} \right)_{T,\, V} \left(\frac{\partial \langle N \rangle}{\partial V} \right)_{T,\, P}^{-1} \right] \qquad (14.22)$$

For a system with a constant number of particles at a constant temperature, we have

$$d \langle N \rangle = \left(\frac{\partial \langle N \rangle}{\partial P} \right)_P dV + \left(\frac{\partial \langle N \rangle}{\partial P} \right)_V dP = 0 \qquad (14.23)$$

and therefore

$$\left(\frac{\partial \langle N \rangle}{\partial P} \right)_{V,\, T} \left(\frac{\partial \langle N \rangle}{\partial V} \right)_{P,\, T}^{-1} = -\left(\frac{\partial V}{\partial P} \right)_{\langle N \rangle,\, T} \qquad (14.24)$$

If we introduce this expression into the formula for $\langle \Delta V^2 \rangle$ we obtain the following expression for the fluctuation of the volume in a system with a constant number of particles provided that the temperature is constant:

$$\langle \Delta V^2 \rangle = -kT \left(\frac{\partial V}{\partial P} \right)_{\langle N \rangle,\, T} \qquad (14.25)$$

It must be stressed that expression (14.25) relates to sufficiently large fluctuations, with respect to which the assumption (14.19) holds. The fluctuating system must also be sufficiently large (contain a sufficiently large number of particles) so that it will pay to apply to it the thermodynamic relations used in the transition from (14.21) to (14.25).

14.3. Fluctuations of the Energy and Temperature

Let us consider the fluctuations of the energy in a system with a fixed number of particles confined in a definite volume V. With a view to the definition of the internal energy and the normalization condition [see (8.20) and (8.21)], we can write

$$\sum_{\nu N} \exp\left(\frac{\Omega^* - \mathcal{E}_{\nu N} + \mu N}{kT}\right)(\mathcal{E}_{\nu N} - U) = 0 \qquad (14.26)$$

Assume that the number of particles in the system is constant, i.e. that $N = \langle N \rangle$. It is therefore convenient to introduce the free energy [see (8.42)]

$$F^* = \Omega^* + \mu\,\langle N \rangle$$

Relation (14.26) acquires the following form:

$$\sum_{\nu} (\mathcal{E}_{\nu} - U) \exp\left(\frac{F^* - \mathcal{E}_{\nu}}{kT}\right) = 0 \qquad (14.27)$$

To find the mean square deviation of the energy from its equilibrium value, i.e. $\langle(\mathcal{E}_{\nu} - U)^2\rangle$, we may differentiate (14.27) with respect to the temperature. The result is

$$\sum_{\nu} (\mathcal{E}_{\nu} - U)\left[\frac{\partial F^*}{\partial T}\frac{1}{kT} - \frac{1}{kT^2}(F^* - \mathcal{E}_{\nu})\right]\exp\left(\frac{F^* - \mathcal{E}_{\nu}}{kT}\right)$$

$$-\frac{\partial U}{\partial T}\sum_{\nu}\exp\left(\frac{F^* - \mathcal{E}_{\nu}}{kT}\right) = 0 \qquad (14.28)$$

Since by (8.46), we have

$$\frac{\partial F^*}{\partial T} = \frac{\partial \Omega^*}{\partial T}$$

it follows from the Gibbs-Helmholtz equation (8.36) that

$$T\,\frac{\partial F^*}{\partial T} - F^* = T\,\frac{\partial \Omega^*}{\partial T} - (\Omega^* + \mu\,\langle N \rangle) = -U$$

and, consequently, (14.28) leads to the equation

$$\sum_{\nu}\frac{1}{kT^2}(\mathcal{E}_{\nu} - U)^2 \exp\left(\frac{F^* - \mathcal{E}_{\nu}}{kT}\right) - \left(\frac{\partial U}{\partial T}\right)_V = 0 \qquad (14.29)$$

Since

$$\langle \Delta \mathscr{E}_v^2 \rangle = \langle (\mathscr{E}_v - U)^2 \rangle = \sum_v (\mathscr{E}_v - U)^2 \exp\left(\frac{F^* - \mathscr{E}_v}{kT}\right)$$

the dispersion of the energy is determined by the following simple relation

$$\langle \Delta \mathscr{E}_v^2 \rangle = kT^2 \left(\frac{\partial U}{\partial T}\right)_V \tag{14.30}$$

Seeing that

$$\left(\frac{\partial U}{\partial T}\right)_V = C_V$$

where C_V is the heat capacity of the system at constant volume, Eq. (14.30) can also be written as

$$\langle \Delta \mathscr{E}_v^2 \rangle = kT^2 C_V \tag{14.31}$$

Formulas (14.30) and (14.31) are exactly the basic relations that determine the magnitude of the energy fluctuation in a system with a constant number of particles at a constant volume.

If a system is at constant volume and the number of particles in it is constant, from the macroscopic viewpoint the change in the internal energy is associated with a change in the system's temperature. In this connection, we can determine the magnitude of the temperature fluctuations from (14.31). Indeed,

$$\Delta U = \left(\frac{\partial U}{\partial T}\right)_V \Delta T = C_V \Delta T \tag{14.32}$$

It is therefore assumed that

$$\langle \Delta \mathscr{E}_v^2 \rangle = C_V^2 \langle \Delta T^2 \rangle \tag{14.33}$$

A comparison of (14.33) with (14.31) shows that

$$\langle \Delta T^2 \rangle = \frac{kT^2}{C_V} \tag{14.34}$$

Let us stop to consider the meaning of the last relation. In Gibbs's theory, the temperature plays the role of a constant parameter characterizing the heat bath in the long run, and therefore we ought to make no mention of temperature fluctuations. In measuring the temperature, however, we must treat the part of a body which the measuring

instrument is in contact with as the heat bath. The inertia of an instrument, i.e. the time it needs for its reading to become stable, also determines the volume of the part of the body in which thermal equilibrium manages to set in during this time. By the heat capacity in (14.34), provided that the heat capacity of the thermometer itself is negligibly small, we must understand just the heat capacity of this part. If the time constant (inertia) of the measuring instrument is such that thermal equilibrium has time to set in in the entire body, the readings of the instrument characterize the fluctuations of the temperature of this body.

14.4. Fluctuations of Other Thermodynamic Quantities

The expressions for $\langle \Delta V^2 \rangle$ and $\langle \Delta T^2 \rangle$ obtained in the preceding two sections allow us to consider the fluctuations of any other thermodynamic quantities occurring in a system with a constant number of particles.

We shall preliminarily note that the fluctuations of the volume and the temperature in the meaning in which they were treated above are statistically independent. This follows from the fact that the volume fluctuations were considered at a constant temperature and in essence were due to fluctuation of the number of particles, whereas the temperature fluctuations were considered at a constant volume and a *constant* number of particles, i.e. were in no way associated with the fluctuations of the number of particles. If we form the product $\Delta V \, \Delta T$ and average it, as a result of the independence of ΔV and ΔT averaging may be performed independently first over ΔV, and then over ΔT. Hence,

$$\langle \Delta V \, \Delta T \rangle = \langle \Delta V \rangle \, \langle \Delta T \rangle$$

Since both the mean value of the volume fluctuation and the mean value of the temperature fluctuation equal zero, we have

$$\langle \Delta V \, \Delta T \rangle = 0 \qquad (14.35)$$

We shall treat the general procedure for calculating the magnitude of fluctuations using pressure fluctuation as an example. Limiting ourselves, as previously, to a treatment of the fluctuations in small, but macroscopic systems, with

respect to which there is a meaning in introducing the concept of pressure, we may consider that the change in the pressure at a constant number of particles is a result of a change in the volume and temperature:

$$\Delta P = \left(\frac{\partial P}{\partial V} \right)_T \Delta V + \left(\frac{\partial P}{\partial T} \right)_V \Delta T$$

Squaring and averaging this relation, we find

$$\langle \Delta P^2 \rangle = \left(\frac{\partial P}{\partial V} \right)_T \langle \Delta V^2 \rangle + 2 \left(\frac{\partial P}{\partial V} \right)_T \left(\frac{\partial P}{\partial T} \right)_V \langle \Delta V \Delta T \rangle$$
$$+ \left(\frac{\partial P}{\partial T} \right)_V^2 \langle \Delta T^2 \rangle$$

or, with a view to the statistical independence of the volume and temperature fluctuations,

$$\langle \Delta P^2 \rangle = \left(\frac{\partial P}{\partial V} \right)_T^2 \langle \Delta V^2 \rangle + \left(\frac{\partial P}{\partial T} \right)_V \langle \Delta T^2 \rangle \qquad (14.36)$$

Substitution into (14.36) of the values for $\langle \Delta V^2 \rangle$ and $\langle \Delta T^2 \rangle$ from (14.25) and (14.34), respectively, yields

$$\langle \Delta P^2 \rangle = \left(\frac{\partial P}{\partial V} \right)_V^2 \left[-kT \left(\frac{\partial V}{\partial P} \right)_T \right] + \left(\frac{\partial P}{\partial T} \right)_V^2 \frac{kT^2}{C_V}$$
$$= kT \left[-\left(\frac{\partial P}{\partial V} \right)_V + \left(\frac{\partial P}{\partial T} \right)_V^2 \frac{T}{C_V} \right] \qquad (14.37)$$

By several cumbersome transformations, which we shall omit, it can be shown that (14.37) is equivalent to the following equation:

$$\langle \Delta P^2 \rangle = -kT \left(\frac{\partial P}{\partial V} \right)_S \qquad (14.38)$$

where $(\partial P / \partial V)_S$ is the derivative of the pressure with respect to the volume at a constant entropy, i.e. in an adiabatic process.

As a second example, let us consider the mean value of the product of the volume and pressure fluctuations. Since

$$\Delta V \, \Delta P = \Delta V \left[\left(\frac{\partial P}{\partial V} \right)_T \Delta V + \left(\frac{\partial P}{\partial T} \right)_V \Delta T \right]$$
$$= \left(\frac{\partial P}{\partial V} \right)_T \Delta V^2 + \left(\frac{\partial P}{\partial T} \right)_V \Delta V \, \Delta T$$

then after averaging, with a view to (14.35), we find

$$\langle \Delta P\, \Delta V \rangle = \left(\frac{\partial P}{\partial V} \right)_T \langle \Delta V^2 \rangle$$

or after inserting the value of $\langle \Delta V^2 \rangle$,

$$\langle \Delta P\, \Delta V \rangle = \left(\frac{\partial P}{\partial V} \right)_T (-kT) \left(\frac{\partial V}{\partial P} \right)_T = -\,kT \quad (14.39)$$

Hence, the pressure and volume fluctuations are not independent. Inspection of (14.39) shows that since the right-hand side is negative, on an average an increase in volume is attended by a decrease in pressure, and vice versa.

It can be shown in a similar way that the pressure and temperature fluctuations are dependent:

$$\langle \Delta P\, \Delta T \rangle = \left(\frac{\partial P}{\partial V} \right)_T \langle \Delta V\, \Delta T \rangle + \left(\frac{\partial P}{\partial T} \right)_V \langle \Delta T^2 \rangle$$

$$= \left(\frac{\partial P}{\partial T} \right)_V \langle \Delta T^2 \rangle = \frac{kT^2}{C_V} \left(\frac{\partial P}{\partial T} \right)_V \quad (14.40)$$

These examples are apparently sufficient to understand the method by means of which it is convenient to evaluate the fluctuations of various thermodynamic quantities.

14.5. Noise Currents

Now we shall consider the practically important matter of noise currents that often determine the limiting sensitivity of modern radio engineering measuring equipment. We shall limit ourselves to a simplified variant of the theory to be able to use simple mathematics.

Assume that the electric current I flows in a conductor of length l and cross-sectional area S. It is said that in this case we have to do with a **current element** Il. To investigate noise, it is convenient to represent a current element in a different form. Since the current is related to the current density by the expression $I = iS$, while the current density, in turn, owing to formulas (3.56) and (3.44), can be written as

$$i = -ej = -en \langle v \rangle \quad (14.41)$$

where n is the concentration of the electrons, and $\langle v \rangle$ is their mean velocity, we have

$$Il = iSl = iV = -e \langle v \rangle nV = -e \langle v \rangle \langle N \rangle \quad (14.42)$$

($V = Sl$ is the volume of the conductor, and $\langle N \rangle = nV$ is the number of electrons in it).

Expression (14.42) can be interpreted from a physical viewpoint as follows. An electron having the charge $-e$ and moving at the velocity v is the current element $-ev$. The current element Il is simply the sum of the current elements of individual electrons. We shall take this proposition as a basic one and shall consider it to be exact, i.e. not only for mean values, but also for instantaneous ones, so that

$$I (t)\, l = \sum_{\alpha} -ev_{\alpha x}$$

where $v_{\alpha x}$ is the instantaneous value of the projection onto the direction of the current (the x-axis) of the velocity for the electron numbered α. The sum is evaluated over all the electrons in the conductor. It follows from the above expression for the instantaneous current that

$$I (t) = -\frac{e}{l} \sum_{\alpha} v_{\alpha x} \qquad (14.43)$$

Our further analysis will be based on this equation.

A glance at (14.43) shows that the current is a random variable, and its randomness is due to two causes. On the one hand, the velocities of electrons have a component due to thermal chaotic motion. On the other hand, the number of electrons in a conductor is also random, so that the number of addends in the sum fluctuates.

Let us calculate the dispersion of the current, which by definition is

$$\langle \Delta I^2 \rangle = \langle [I (t) - \langle I \rangle]^2 \rangle$$

With the help of (14.43) we obtain for the dispersion

$$\langle \Delta I^2 \rangle = \left\langle \left[\frac{e}{l} \sum_{\alpha} v_{\alpha x} - \frac{e}{l} \langle v_{\alpha x} \rangle \langle N \rangle \right]^2 \right\rangle \qquad (14.44)$$

In assuming that a current flows in a conductor, we must consider that the velocity of the α-th electron can be written as

$$v_{\alpha x} = \langle v_{\alpha x} \rangle + \Delta v_{\alpha x} \qquad (14.45)$$

where $\langle v_{\alpha x} \rangle$ is the mean value of the velocity (non-zero because a current is present), and $\Delta v_{\alpha x}$ is the random thermal

velocity. The mean value of the thermal velocity is natu-
rally zero and, in addition, the thermal velocities of differ-
ent electrons are independent. After inserting (14.45) into
(14.43), we obtain the following expression for the current
dispersion:

$$\langle \Delta I^2 \rangle = \frac{e^2}{l^2} \left\langle \left[\sum_\alpha \left(\langle v_{\alpha x} \rangle + \Delta v_{\alpha x} \right) - \langle v_{\alpha x} \rangle \langle N \rangle \right]^2 \right\rangle$$

$$= \frac{e^2}{l^2} \left\langle \left[\sum_\alpha \langle v_{\alpha x} \rangle + \sum_\alpha \Delta v_{\alpha x} - \langle v_{\alpha x} \rangle \langle N \rangle \right]^2 \right\rangle \qquad (14.46)$$

The sum $\sum_\alpha \langle v_{\alpha x} \rangle$ equals $\langle v_{\alpha x} \rangle N$, where N is the instan-
taneous value of the number of electrons. Assume that

$$N = \langle N \rangle + \Delta N$$

so that ΔN is the deviation of the number of electrons
from the mean value. Expression (14.46) now becomes

$$\langle \Delta I^2 \rangle = \frac{e^2}{l^2} \left\langle \left[\langle N \rangle \langle v_{\alpha x} \rangle + \Delta N \langle v_{\alpha x} \rangle \right. \right.$$

$$\left. \left. + \sum_\alpha \Delta v_{\alpha x} - \langle v_{\alpha x} \rangle \langle N \rangle \right]^2 \right\rangle$$

or, after collecting terms,

$$\langle \Delta I^2 \rangle = \frac{e^2}{l^2} \left\langle \left[\langle v_{\alpha x} \rangle \Delta N + \sum_\alpha \Delta v_{\alpha x} \right]^2 \right\rangle \qquad (14.47)$$

The fluctuations of the number of electrons and the
fluctuations of the velocity of the electrons are independent,
therefore the mean values of the products $\Delta v_{\alpha x} \Delta N$ are
zero. This allows us to write, after squaring and averaging,
that

$$\langle \Delta I^2 \rangle = \frac{e^2}{l^2} \left[\langle v_{\alpha x} \rangle^2 \langle \Delta N^2 \rangle + \left\langle \left(\sum_\alpha \Delta v_{\alpha x} \right)^2 \right\rangle \right]$$

If we also have in view the independence of the velocities
of different electrons, it is a simple matter to obtain by
averaging velocities

$$\left\langle \left(\sum_\alpha \Delta v_{\alpha x} \right)^2 \right\rangle = \sum_\alpha \langle \Delta v_{\alpha x}^2 \rangle = N \langle \Delta v_{\alpha x}^2 \rangle$$

Now let us average over the number of electrons. We have

$$\langle \Delta I^2 \rangle = \frac{e^2}{l^2} \langle v_{\alpha x} \rangle^2 \langle \alpha N^2 \rangle + \frac{e^2}{l^2} \langle N \rangle \langle \Delta v_{\alpha x}^2 \rangle \qquad (14.48)$$

Examination of (14.48) reveals that the current dispersion consists of two components. One of them is associated with the fluctuations of the velocities of the electrons and is called the **thermal** or **Johnson noise**. It does not depend on the current (on the velocity of directed motion), and therefore also occurs when no current flows in a conductor. The second component is called the **shot, Schottky, or fluctuation noise**. It is associated with the fluctuation of the number of electrons and manifests itself only when a current flows in a conductor. It is sometimes called the generation-recombination noise depending on what causes the fluctuation in the number of particles.

Let us obtain more convenient expressions for both components of the noise current.

The mean-square value of the fluctuation noise, as can be seen from (14.48), is

$$\langle \Delta I_{fl}^2 \rangle = \frac{e^2}{l^2} \langle v_{\alpha x} \rangle^2 \langle \Delta N^2 \rangle \qquad (14.49)$$

When we may consider that

$$\langle \Delta N^2 \rangle = nV$$

(in particular in a conductor whose length is smaller than the Debye length), it follows from (14.49) that

$$\langle \Delta I_{fl}^2 \rangle = \frac{e^2}{l^2} \langle v_{\alpha x} \rangle^2 \, nV = e \, \frac{e \langle v_{\alpha x} \rangle \, n}{l / \langle v_{\alpha x} \rangle} \, \frac{V}{l} \qquad (14.50)$$

Since $V/l = S$ is the cross section of a conductor, and $l/\langle v_{\alpha x} \rangle = t_0$ is the time of flight, i.e. the time during which an electron travels through the conductor, then with account taken of (14.41), we find from (14.50) that

$$\langle \Delta I_{fl}^2 \rangle = e \, \frac{iS}{t_0} = e \, \frac{I}{t_0} \qquad (14.51)$$

From a physical viewpoint, the fluctuation component of the noise can be interpreted as follows. Every electron when moving in a conductor at the mean velocity $\langle v_{\alpha x} \rangle$ produces a current pulse with a duration equal to the time

of flight[*]. The current pulses of individual electrons are random in the respect that the instant of their appearance is random.

To determine the reaction of the circuits and instruments connected to a conductor to fluctuation noise, it will be expedient to go over to a **spectral representation**, i.e. represent a current pulse in the form of a sum of sinusoidal signals. We can obtain such a representation by using the Fourier expansion. The spectral representation simplifies our treatment because it is a simple matter to calculate the passage of a sinusoidal signal through an electric circuit if the frequency characteristic of the circuit is known.

It is known from the theory of the Fourier expansion that the spectral density $S(\omega)$ of a current pulse whose form is determined by the function $f(t)$ is calculated by the formula (see [19], p. 544)

$$S(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} f(t)\, e^{-i\omega t}\, dt$$

In the given case, having in view the rectangular shape of a current pulse whose amplitude we designate by A and choosing the instant $t = 0$ at the middle of a pulse, we obtain

$$S(\omega) = \frac{1}{2\pi} \int_{-t_0/2}^{+t_0/2} A\, e^{-i\omega t}\, dt$$

Evaluation of this integral yields

$$S(\omega) = \frac{A}{2\pi} \frac{e^{i\omega t_0/2} - e^{-i\omega t_0/2}}{i\omega} = \frac{A}{2\pi}\, t_0\, \frac{\sin(\omega t_0/2)}{\omega t_0/2}$$

The energy of the spectral component with the frequency ω is proportional to the square of the magnitude of the spectral density at this frequency:

$$|S(\omega)|^2 = \frac{A^2 t_0^2}{4\pi^2} \frac{\sin^2(\omega t_0/2)}{(\omega t_0/2)^2} \qquad (14.52)$$

---

[*] For a generation-recombination noise, the duration of the individual pulses is determined not so much by the time of flight as by what is called the lifetime of an electron, i.e. the mean time of its existence, which is usually much smaller than the time of flight.

A plot of this function is shown in Fig. 14.2. It reaches a maximum value at zero frequency and gradually diminishes with an increasing absolute value of the frequency. At $\omega = 2\pi/t_0$, the function becomes equal to zero for the first time, and after this its value is very small. At $\omega = 0$, we have

$$| S(0) |^2 = \frac{A^2 t_0^2}{4\pi^2}$$

It is convenient to introduce the concept of the frequency band in which the fluctuation noise is non-zero. To do this, the real function $| S(\omega) |^2$ is replaced with a rectangle
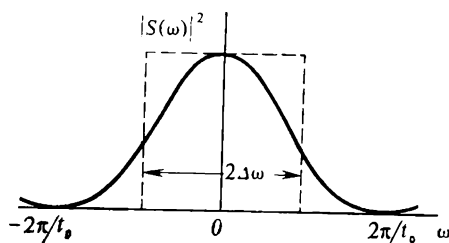
Fig. 14.2

as shown by the dashed line in Fig. 14.2. The altitude of the rectangle equals the square of the magnitude of the spectral density $| S(0) |^2$ at the peak, and a width is chosen such that the area of the rectangle would equal the area under the curve $| S(\omega) |^2$. The width is designated by $2\Delta\omega$ because only positive frequencies have a physical meaning. Mathematically, the equality of the areas is written as follows:

$$2 \Delta\omega \, | S(0) |^2 = \int\limits_{-\infty}^{+\infty} | S(\omega) |^2 \, d\omega$$

Since

$$\int\limits_{-\infty}^{+\infty} | S(\omega) |^2 \, d\omega = | S(0) |^2 \int\limits_{-\infty}^{+\infty} \frac{\sin^2 (\omega t_0/2)}{(\omega t_0/2)^2} \, d\omega$$

$$= | S(0) |^2 \frac{2}{t_0} \int\limits_{-\infty}^{+\infty} \frac{\sin^2 y}{y^2} \, dy$$

and*

$$\int\limits_{-\infty}^{+\infty} \frac{\sin^2 y}{y^2}\, \mathrm{d}y = \pi$$

we have

$$2\,\Delta\omega = \frac{2\pi}{t_0}$$

If instead of the cyclic frequency ω we introduce the ordinary one f, we obtain the following expression for the frequency band in which the fluctuation noise is non-zero:

$$\Delta f_{\mathrm{fl}} = \frac{1}{2t_0} \qquad (14.53)$$

Hence, for the fluctuation noise, we have

$$\langle \Delta I_{\mathrm{fl}}^2 \rangle = 2eI\,\Delta f_{\mathrm{fl}}$$

A device connected to a conductor with noise may fail to react to all the frequencies contained in the spectrum of fluctuation noise. If it transmits the frequency band Δf falling to the range of frequencies near the maximum of the spectral sensitivity, i.e. to frequencies much smaller than $f = 1/t_0$ at which the spectral density vanishes, the noise is determined by the power of the transmitted spectral components. The power of the noise that has passed through the device, proportional to the square of the current, is less than the total power of the fluctuation noise by the same number of times by which the band Δf of the device is less than the band Δf_{fl}. Hence, *the fluctuation noise acting on an instrument connected to a conductor has the dispersion*

$$\langle \Delta I_{\mathrm{fl}}^2 \rangle = 2eI\,\Delta f \qquad (14.53)$$

that is proportional to the current in the conductor and the frequency band of the instrument.

---

* Integration by parts yields

$$\int\limits_{-\infty}^{+\infty} \frac{\sin^2 y}{y^2}\, \mathrm{d}y = -\frac{\sin^2 y}{y}\Big|_{-\infty}^{+\infty} + \int\limits_{-\infty}^{+\infty} \frac{2\sin y\cos y}{y}\, \mathrm{d}y$$

$$= \int\limits_{-\infty}^{+\infty} \frac{\sin 2y}{y}\, \mathrm{d}y$$

The value of the last integral is π (see, for example, [19], p. 408).

The passing of a random current in a conductor having the resistance R causes a random voltage to appear across it. The mean-square value of this voltage can readily be obtained by multiplying (14.53) by the square of the resistance:

$$\langle \Delta U_{fl}^2 \rangle = R^2 \langle \Delta I_{fl}^2 \rangle = 2eIR^2 \, \Delta f \qquad (14.54)$$

The power of the fluctuation noise in a conductor is determined by the formula

$$P = \langle \Delta I_{fl}^2 \rangle R = 2eIR \, \Delta f$$

Let us now pass over to thermal noise. The dispersion of the thermal noise current by (14.48) is

$$\langle \Delta I_{th}^2 \rangle = \frac{e^2}{l^2} \langle N \rangle \langle \Delta v_{\alpha x}^2 \rangle$$

Since $\langle v_{\alpha x}^2 \rangle = kT/m_0$, and the mean number of particles $\langle N \rangle = nV$, we have

$$\langle \Delta I_{th}^2 \rangle = \frac{e^2}{l^2} \, Vn \, \frac{kT}{m_0} \qquad (14.55)$$

Assume that from one collision to another the electrons travel the same time τ regardless of their velocity. The
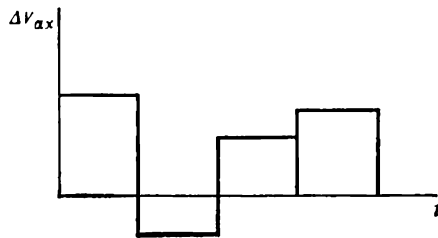
Fig. 14.3

projection of the thermal velocity of an individual electron onto the x-axis as a function of time therefore has the form shown in Fig. 14.3, i.e. the current produced by a given electron is a sequence of pulses of the same duration, but of different amplitudes.

In the model being considered, the mobility of the electrons is equal to

$$\eta = \frac{e\tau}{2m_0} \qquad (14.56)$$

Indeed, an electron moves in the field E with the acceleration $a = -eE/m_0$. Its velocity grows from zero after a collision to

$$v = a\tau = -\frac{eE\tau}{m_0}$$

before the next collision, after which it again loses its directed velocity. The mean drift velocity is thus equal to

$$\langle v \rangle = \frac{v+0}{2} = \frac{v}{2} = -\frac{eE\tau}{2m_0} = -\eta E$$

whence formula (14.56) follows.

If we multiply and divide (14.55) by τ we can write

$$\langle \Delta I_{\text{th}}^2 \rangle = \frac{e^2 n V \, kT \, \tau}{l^2 m_0 \tau} = 2\,\frac{e\tau}{2m_0}\, en\, \frac{V}{l^2}\, \frac{kT}{\tau} = 2\mu en\, \frac{V}{l^2}\, \frac{kT}{\tau}$$

Introducing the conductivity $\sigma = \eta en$, we have

$$\langle \Delta I_{\text{th}}^2 \rangle = 2\sigma\, \frac{kT}{l^2}\, V\, \frac{1}{\tau} = 2\,\frac{kT}{l^2/(\sigma V)}\, \frac{1}{\tau} \qquad (14.57)$$

Since the resistance of a conductor is

$$R = \frac{l}{\sigma S} = \frac{l^2}{\sigma V}$$

we can write (14.57) in the form

$$\langle \Delta I_{\text{th}}^2 \rangle = 2\,\frac{kT}{R}\, \frac{1}{\tau}$$

Random pulses of thermal current are assumed to have the same duration, therefore, the transition to a spectral representation is accomplished in exactly the same way as for a drift current. The result is

$$\langle \Delta I_{\text{th}}^2 \rangle = 4\,\frac{kT}{R}\, \Delta f_{\text{th}}$$

where $\Delta f_{\text{th}} = 1/2\tau$ is the thermal noise frequency band. Since τ is very small (of the order of 10^{-12} s at room temperature), the thermal noise spectrum is virtually uniform from the zero frequency to very high frequencies of the order of $1/\tau$. These frequencies correspond to the millimetre wavelength band. Taking account in exactly the same way as before of the role played by the transmission band of the instrument, we find for the magnitude of the thermal

noise acting on an instrument with the transmission band Δf

$$\langle \Delta I^2_{\text{th}} \rangle = 4 \frac{kT}{R} \Delta f \qquad (14.58)$$

For the mean value of the square of the thermal noise voltage, we obtain

$$\langle \Delta U^2_{\text{th}} \rangle = 4kTR\ \Delta f \qquad (14.59)$$

and for the power of the thermal noise

$$P = 4kT\ \Delta f \qquad (14.60)$$

The last three formulas determining the magnitude of the thermal noise in an electric circuit are known as the **Nyquist formulas**.

APPENDICES

1. Probability Integral (Error Function) at Small and Large Values of the Argument

When $x_0 \leqslant 1$, the variable x in the integral

$$\text{erf}(x_0) = \frac{2}{\sqrt{2\pi}} \int_0^{x_0} e^{-x^2/2} \, dx$$

being less than x_0, is also less than unity, and the exponential can be expanded into a rapidly converging series. We thus have

$$\text{erf}(x_0) = \frac{2}{\sqrt{2\pi}} \int_0^{x_0} \left[1 - \frac{x^2}{2} + \frac{1}{2} \left(\frac{x^2}{2} \right)^2 - \ldots \right] dx$$

$$= \frac{2}{\sqrt{2\pi}} \left(x_0 - \frac{x_0^3}{6} + \frac{x_0^5}{40} - \ldots \right) \tag{A.1}$$

If we limit ourselves to the first term of the series, we have

$$\text{erf}(x_0) = \sqrt{\frac{2}{\pi}} \, x_0 \tag{A.2}$$

and, as can be seen from (A.1), the error when $x_0 \leqslant 1$ is less than 1/6, i.e. 15%. Taking two terms into account ensures an accuracy of 2.5%.

When $x_0 \gg 1$, the error function is estimated in a different way. Let us write the following expression:

$$\text{erf}(x_0) = 1 - \sqrt{\frac{2}{\pi}} \int_{x_0}^{\infty} e^{-x^2/2} \, dx \tag{A.3}$$

If x_0 is large, the integral is small, and $\text{erf}(x_0)$ is close to unity. Let us transform (A.3) as follows

$$\text{erf}(x_0) = 1 - \sqrt{\frac{2}{\pi}} \int_{x_0}^{\infty} \frac{1}{x} e^{-x^2/2} \, d\left(\frac{x^2}{2} \right)$$

$$= 1 + \int_{x_0}^{\infty} \sqrt{\frac{2}{\pi}} \frac{1}{x} \, d(e^{-x^2/2}) \tag{A.4}$$

If we now integrate by parts, we have

$$\sqrt{\frac{2}{\pi}} \int_{x_0}^{\infty} \frac{1}{x} \, d\,(e^{-x^2/2}) = -\sqrt{\frac{2}{\pi}} \frac{1}{x_0} e^{-x_0^2/2}$$

$$+ \sqrt{\frac{2}{\pi}} \int_{x_0}^{\infty} \frac{1}{x^2} e^{-x^2/2} \, dx \qquad (A.5)$$

The last integral on the right-hand side owing to the factor x^{-2} is at least x_0^{-2} times smaller than the initial one. Consequently, if x_0 is large, then

$$\sqrt{\frac{2}{\pi}} \int_{x_0}^{\infty} e^{-x^2/2} \, dx \approx \sqrt{\frac{2}{\pi}} \frac{1}{x_0} e^{-x_0^2/2}$$

and, therefore,

$$\text{erf}\,(x_0) = 1 - \frac{2}{\sqrt{2\pi}} \frac{1}{x_0} e^{-x_0^2/2} \qquad (A.6)$$

with an error of the order of

$$\frac{2}{\sqrt{2\pi}} \frac{1}{x_0^3} e^{-x_0^2/2}$$

When $x_0 > 2$, formula (A.6) ensures an accuracy that is adequate in the majority of practical calculations.

2. Evaluation of Some Frequently Encountered Integrals

It will pay to consider the evaluation of the integral

$$I\,(\beta) = \int_{-\infty}^{+\infty} \exp\,(-\beta p_x^2) \, dp_x \qquad (A.7)$$

in greater detail because together with quite a few other close integrals, it is often encountered in statistics. It is much more convenient to calculate not $I\,(\beta)$, but the square of this integral. Since the integration variable may be designated in any way, we have

$$I^2\,(\beta) = \int_{-\infty}^{+\infty} \exp\,(-\beta x^2) \, dx \int_{-\infty}^{+\infty} \exp\,(-\beta y^2) \, dy \qquad (A.8)$$

The product of the integrals can be represented as one double integral that is evaluated over the entire plane (x, y):

$$I^2\,(\beta) = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \exp\,[-\beta\,(x^2 + y^2)] \, dx \, dy \qquad (A.9)$$

Further calculations are simplified if we go over to polar coordinates on a plane. Since

$$x^2 + y^2 = \rho^2 \qquad (A.10)$$

where ρ is the distance to a point with the coordinates x and y from the origin of coordinates, and an element of area dS in the polar system has the form

$$dS = \rho \, d\rho \, d\varphi$$

(φ is the polar angle), we have

$$I^2(\beta) = \int_0^\infty \int_0^{2\pi} \exp(-\beta\rho^2) \, \rho \, d\rho \, d\varphi$$

Integration is performed over the entire plane, and thus ρ varies from 0 to ∞ and the angle φ from 0 to 2π. The integral over φ yields 2π, and therefore

$$I^2(\beta) = 2\pi \int_0^\infty \exp(-\beta\rho^2) \, \rho \, d\rho = \frac{\pi}{\beta}$$

that is

$$I(\beta) = \sqrt{\frac{\pi}{\beta}} \qquad (A.11)$$

It is a simple matter to find the values of a number of other integrals encountered in statistics with the aid of the evaluated one. For instance, if we differentiate the identity

$$\sqrt{\frac{\pi}{\beta}} = \int_{-\infty}^{+\infty} \exp(-\beta p_x^2) \, dp_x$$

with respect to β, we obtain

$$-\frac{\sqrt{\pi}}{2} \beta^{-3/2} = -\int_{-\infty}^{+\infty} p_x^2 \exp(-\beta p_x^2) \, dp_x \qquad (A.12)$$

Differentiating (A.12) with respect to β again, we find

$$\frac{3}{4} \sqrt{\pi} \beta^{-5/2} = \int_{-\infty}^{+\infty} p_x^4 \exp(-\beta p_x^2) \, dp_x$$

and so on. In this way, it is not difficult to obtain the values of the following integrals:

$$\int_{-\infty}^{+\infty} p_x^{2n} \exp(-\beta p_x^2) \, dp_x = \sqrt{\frac{\pi}{\beta^{2n-1}}} \frac{1 \times 3 \times 5 \dots (2n-1)}{2^n} \qquad (A.13)$$

3. Theorem on the Uniform Distribution of the Kinetic Energy among the Degrees of Freedom

Let us consider the proof of the theorem on the uniform distribution of the kinetic energy among the degrees of freedom. Let the position of a system in space be determined by $3N$ coordinates. Since these coordinates may include not only the distances measured along the axes of a Cartesian coordinate system, but also other quantities such as, for example, the angle of rotation in the rotation of a rigid body, we shall call them **generalized coordinates** and designate them by q_i. If the minimum number of generalized coordinates q_1, q_2, ..., q_{3N} needed to completely determine the position of a system in space is $3N$, the number of degrees of freedom of the system is said
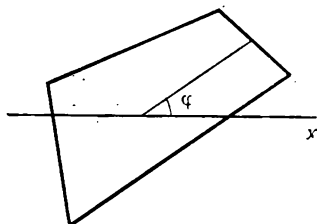
Fig. A.1

to equal $3N$. For example, the position of a rigid body fixed on a stationary axis about which it can rotate is determined by only a single coordinate, most conveniently, by the angle of rotation φ. If the axis of rotation is chosen as the z-axis, the angle of rotation φ can be measured from a certain direction taken as the x-axis as shown in Fig. A.1. The angle φ is the generalized coordinate of the given system which thus has one degree of freedom.

The time derivative of the generalized coordinate is said to be the **generalized velocity**. In the above example, the generalized velocity coincides with the angular velocity of rotation ω:

$$\dot{\varphi} = \omega$$

The Cartesian coordinates of any point of a system are uniquely determined by the generalized coordinates, and therefore its velocity is a linear function of the generalized velocities. Indeed, let the Cartesian coordinate x_i of one of the points of the system be a function of the generalized coordinates q_1, q_2, . . ., q_{3N}

$$x_i = f_i (q_1, q_2, \ldots, q_{3N}) \qquad (A.14)$$

consequently,

$$v_{ix} = \dot{x}_i = \frac{\partial f_i}{\partial q_1}\, \dot{q}_1 + \frac{\partial f_i}{\partial q_2}\, \dot{q}_2 + \ldots + \frac{\partial f_i}{\partial q_{3N}}\, \dot{q}_{3N} = \sum_{j=1}^{3N} \frac{\partial f_i}{\partial q_j}\, \dot{q}_j \qquad (A.15)$$

where the derivatives $\partial f_i / \partial q_j$, although they do depend on the generalized coordinates, do not depend on their derivatives, i.e. on the generalized velocities. For example, for the points of a rigid body rotating about the z-axis, we have

$$x_i = r_i \cos \varphi \quad \text{and} \quad y_i = r_i \sin \varphi \tag{A.16}$$

where r_i is the distance to the point i from the axis of rotation and therefore

$$\left.\begin{array}{l} v_{ix} = \dot{x}_i = -(r_i \sin \varphi)\,\dot{\varphi} \\[2mm] v_{iy} = \dot{y}_i = (r_i \cos \varphi)\,\dot{\varphi} \end{array}\right\} \tag{A.17}$$

The kinetic energy of the system is

$$\mathscr{E}_\mathbf{k} = \sum_i \left(\frac{m_i v_{ix}^2}{2} + \frac{m_i v_{iy}^2}{2} + \frac{m_i v_{iz}^2}{2} \right) \tag{A.18}$$

If we insert into (A.18) the values of the velocity components expressed in terms of the generalized velocities according to (A.15), the kinetic energy will be found to be a homogeneous quadratic function of the generalized velocities, i.e. it has the form

$$\mathscr{E}_\mathbf{k} = \sum_{i,\,j} a_{ij} \dot{q}_i \dot{q}_j \tag{A.19}$$

where a_{ij} are coefficients that, generally speaking, may depend on the generalized coordinates (but not on the generalized velocities). For a rigid body rotating about the stationary axis z,

$$\mathscr{E}_\mathbf{k} = \sum_i \frac{m_i}{2} (v_{ix}^2 + v_{iy}^2)$$

where m_i is the mass of the i-th element in its composition. Introducing the values of the velocities from A.17, we find an expression for the kinetic energy in terms of the generalized velocity:

$$\mathscr{E}_\mathbf{k} = \sum_i \frac{m_i r_i^2}{2} \dot{\varphi}^2 = I \frac{\dot{\varphi}^2}{2} \tag{A.20}$$

where

$$I = \sum_i m_i r_i^2$$

is the moment of inertia of the rigid body relative to the axis of rotation. Hence, in the given specific case there is one degree of freedom and a single coefficient a_{11} in (A.19) equal to half the moment of inertia.

The momentum of a point particle in the system can be written as follows:

$$p_{ix} = m_i v_{ix} = \frac{\partial}{\partial v_{ix}} \left(\frac{m_i v_{ix}^2}{2} \right) = \frac{\partial}{\partial v_{ix}} \sum_j \frac{m_j v_j^2}{2} = \frac{\partial \mathscr{E}_\mathbf{k}}{\partial v_{ix}} \tag{A.21}$$

By analogy with (A.21), the generalized momentum p_i is defined to be the derivative of the kinetic energy of the system with respect to the generalized velocity:

$$p_i = \frac{\partial \mathscr{E}_k}{\partial \dot{q}_i} = \sum_j a_{ij}\dot{q}_j \tag{A.22}$$

A glance at (A.22) shows that the generalized momentum is a linear function of the generalized velocities. For this reason, conversely, the generalized velocity can be represented as a linear function of the generalized momenta. For instance, for the rotation of a rigid body about a stationary axis, the generalized momentum is

$$p = \frac{\partial \mathscr{E}_k}{\partial \dot{\varphi}} = \frac{\partial}{\partial \dot{\varphi}} \left(\frac{I\dot{\varphi}^2}{2} \right) = I\dot{\varphi} = I\omega \tag{A.23}$$

i.e. it is the angular momentum.

If we express the generalized velocities in terms of the momenta with the aid of Eq. (A.22)

$$\dot{q}_j = \sum_i A_{ji}p_i \tag{A.24}$$

and insert the expression obtained into (A.19), the kinetic energy will be a homogeneous quadratic function of the generalized momenta, i.e. it will have the form

$$\mathscr{E}_k = \sum_{i,j} b_{ij}p_ip_j \tag{A.25}$$

For the example being considered, we find from (A.23) that

$$\dot{\varphi} = \omega = \frac{p}{I}$$

and by (A.20)

$$\mathscr{E}_k = \frac{I}{2}\frac{p^2}{I^2} = \frac{p^2}{2I} \tag{A.26}$$

so that the single coefficient b_{11} is

$$b_{11} = \frac{1}{2I}$$

Since the kinetic energy is a homogeneous quadratic function, according to the Euler theorem, the following identity holds:

$$\mathscr{E}_k = \frac{1}{2}\sum_i p_i \frac{\partial \mathscr{E}_k}{\partial p_i} \tag{A.27}$$

This relation of classical mechanics underlies the derivation of the theorem on the uniform distribution of the kinetic energy among the degrees of freedom.

The kinetic energy falling to the i-th degree of freedom is given by the addend of expression (A.27) having the subscript i:

$$\mathscr{E}_{ki} = \frac{1}{2}\, p_i\, \frac{\partial \mathscr{E}_k}{\partial p_i} \qquad (A.28)$$

For the mean value of the kinetic energy falling to the i-th degree of freedom, we must write in accordance with the Gibbs distribution that

$$\langle \mathscr{E}_{ki} \rangle = \int \mathscr{E}_{ki}\, d\omega = \int \frac{1}{2}\, p_i\, \frac{\partial \mathscr{E}_k}{\partial p_i}\, e^{(F-\mathscr{E})/(kT)}\, d\Gamma \qquad (A.29)$$

The total energy of the system $\mathscr{E}$ is the sum of the kinetic and the potential energies, but since the potential energy does not depend on the velocities and, consequently, on the momenta, we have

$$\frac{\partial \mathscr{E}_k}{\partial p_i} = \frac{\partial (\mathscr{E}_k + \mathscr{E}_p)}{\partial p_i} = \frac{\partial \mathscr{E}}{\partial p_i}$$

This allows us to rewrite (A.29) in the form

$$\langle \mathscr{E}_{ki} \rangle = \int \frac{1}{2}\, p_i\, \frac{\partial \mathscr{E}}{\partial p_i}\, e^{(F-\mathscr{E})/(kT)}\, d\Gamma \qquad (A.30)$$

where $d\Gamma$ is a phase space volume element:

$$d\Gamma = dx_1\, dy_1\, dz_1\, dx_2\, dy_2\, dz_2\, \ldots\, dx_N dy_N\, dz_N$$
$$\times\, dp_{x1}\, dp_{y1}\, dp_{z1}\, dp_{x2}\, dp_{y2}\, dp_{z2}\, \ldots\, d\, p_{xN} d\, p_{yN}\, d\, p_{zN}$$

It is easier to perform integration if we pass over from Cartesian coordinates and momenta to generalized ones. It is known from mathematics that this transition is accomplished according to the rule

$$d\Gamma = J\, dq_1\, \ldots\, dq_{3N}\, dp_1\, \ldots\, dp_{3N} \qquad (A.31)$$

where

$$J = \frac{\partial\, (x_1 y_1 z_1\, \ldots\, x_N y_N z_N p_{x1} p_{y1} p_{z1}\, \cdots\, p_{xN} p_{yN} p_{zN})}{\partial\, (q_1\, \cdots\, q_{3N},\ p_1\, \cdots\, q_{3N})}$$

$$= \begin{vmatrix} \dfrac{\partial x_1}{\partial q_1} & \cdots & \dfrac{\partial x_1}{\partial q_{3N}} & \dfrac{\partial x_1}{\partial p_1} & \cdots & \dfrac{\partial x_1}{\partial p_{3N}} \\ \cdot\ \cdot & & \cdot\ \cdot & \cdot\ \cdot & & \cdot\ \cdot \\ \dfrac{\partial z_N}{\partial q_1} & \cdots & \dfrac{\partial z_N}{\partial q_{3N}} & \dfrac{\partial z_N}{\partial p_1} & \cdots & \dfrac{\partial z_N}{\partial p_{3N}} \\[4pt] \hline \dfrac{\partial p_{x1}}{\partial q_1} & \cdots & \dfrac{\partial p_{x1}}{\partial q_{3N}} & \dfrac{\partial p_{x1}}{\partial p_1} & \cdots & \dfrac{\partial p_{x1}}{\partial p_{3N}} \\ \cdot\ \cdot & & \cdot\ \cdot & \cdot\ \cdot & & \cdot\ \cdot \\ \dfrac{\partial p_{zN}}{\partial q_1} & \cdots & \dfrac{\partial p_{zN}}{\partial q_{3N}} & \dfrac{\partial p_{zN}}{\partial p_1} & \cdots & \dfrac{\partial p_{zN}}{\partial p_{3N}} \end{vmatrix} \qquad (A.32)$$

is a determinant known as the **Jacobian.**

Since by (A.14), the Cartesian coordinates depend only on the generalized coordinates, all the derivatives with respect to the generalized momenta in the top right-hand corner of (A.32) separated by dotted lines vanish. In this connection, the Jacobian is divided into the product of two determinants:

$$J = \begin{vmatrix} \dfrac{\partial x_1}{\partial q_1} & \cdots & \dfrac{\partial x_1}{\partial q_{3N}} \\ \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \\ \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \\ \dfrac{\partial z_N}{\partial q_1} & \cdots & \dfrac{\partial z_N}{\partial q_{3N}} \end{vmatrix} \begin{vmatrix} \dfrac{\partial p_{x1}}{\partial p_1} & \cdots & \dfrac{\partial p_{x1}}{\partial p_{3N}} \\ \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \\ \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \\ \dfrac{\partial p_{zN}}{\partial p_1} & \cdots & \dfrac{\partial p_{zN}}{\partial p_{3N}} \end{vmatrix} \qquad (A.33)$$

It can be shown that the product in (A.33) equals unity. For this purpose, in expression (A.21)

$$p_i = \frac{\partial \acute{\mathscr{e}}_k}{\partial \dot{q}_i}$$

we consider the kinetic energy to be a function of the Cartesian variables:

$$p_i = \frac{\partial \acute{\mathscr{e}}_k}{\partial v_{x1}} \frac{\partial v_{x1}}{\partial \dot{q}_i} + \cdots + \frac{\partial \acute{\mathscr{e}}_k}{\partial v_{zN}} \frac{\partial v_{zN}}{\partial \dot{q}_i}$$

$$= p_{x1} \frac{\partial v_{x1}}{\partial \dot{q}_i} + \cdots + p_{zN} \frac{\partial v_{zN}}{\partial \dot{q}_i}$$

Examination of the above relation shows that

$$\frac{\partial v_{x1}}{\partial \dot{q}_i} = \frac{\partial p_i}{\partial p_{x1}}, \quad \cdots, \quad \frac{\partial v_{zN}}{\partial \dot{q}_i} = \frac{\partial p_i}{\partial p_{zN}}$$

On the other hand, it follows from (A.15) and similar relations after differentiation with respect to q_i that

$$\frac{\partial v_{x1}}{\partial \dot{q}_i} = \frac{\partial x}{\partial q_i}, \quad \cdots, \quad \frac{\partial v_{zN}}{\partial \dot{q}_i} = \frac{\partial z_N}{\partial q_i}$$

and therefore

$$\frac{\partial p_i}{\partial p_{x1}} = \frac{\partial x}{\partial q_i}, \quad \cdots, \quad \frac{\partial p_i}{\partial p_{zN}} = \frac{\partial z_N}{\partial q_i}$$

Hence, the first determinant in (A.33) can be written as follows:

$$\begin{vmatrix} \dfrac{\partial p_1}{\partial p_{x1}} & \cdots & \dfrac{\partial p_{3N}}{\partial p_{x1}} \\ \cdot \cdot \cdot \cdot \cdot \cdot \cdot \\ \cdot \cdot \cdot \cdot \cdot \cdot \cdot \\ \dfrac{\partial p_1}{\partial p_{zN}} & \cdots & \dfrac{\partial p_{3N}}{\partial p_{zN}} \end{vmatrix}$$

Transferring the rows and columns in it, which does not change the value of the determinant, we can write the Jacobian (A.33) as

$$J = \begin{vmatrix} \dfrac{\partial p_1}{\partial p_{x1}} & \cdots & \dfrac{\partial p_1}{\partial p_{zN}} \\ \cdot & \cdot & \cdot \cdot \cdot \cdot \cdot \\ \cdot & \cdot & \cdot \cdot \cdot \cdot \cdot \\ \dfrac{\partial p_{3N}}{\partial p_{x1}} & \cdots & \dfrac{\partial p_{3N}}{\partial p_{zN}} \end{vmatrix} \begin{vmatrix} \dfrac{\partial p_{x1}}{\partial p_1} & \cdots & \dfrac{\partial p_{x1}}{\partial p_{3N}} \\ \cdot & \cdot & \cdot \cdot \cdot \cdot \cdot \\ \cdot & \cdot & \cdot \cdot \cdot \cdot \cdot \\ \dfrac{\partial p_{zN}}{\partial p_1} & \cdots & \dfrac{\partial p_{zN}}{\partial p_{3N}} \end{vmatrix} \quad \text{(A.34)}$$

If we now perform multiplication according to the rule "row by column", we have

$$J = \begin{vmatrix} \dfrac{\partial p_1}{\partial p_1} & \dfrac{\partial p_1}{\partial p_2} & \dfrac{\partial p_1}{\partial p_{3N}} \\ \cdot & \cdot & \cdot \cdot \cdot \cdot \cdot \cdot \cdot \\ \cdot & \cdot & \cdot \cdot \cdot \cdot \cdot \cdot \cdot \\ \dfrac{\partial p_{3N}}{\partial p_1} & \dfrac{\partial p_{3N}}{\partial p_2} & \cdots & \dfrac{\partial p_{3N}}{\partial p_{3N}} \end{vmatrix}$$

i.e. actually

$$J = \begin{vmatrix} 1 & 0 & \ldots & 0 \\ 0 & 1 & \ldots & 0 \\ \cdot & \cdot & \cdot \cdot \cdot & \cdot \\ \cdot & \cdot & \cdot \cdot \cdot & \cdot \\ \cdot & \cdot & \cdot \cdot \cdot & \cdot \\ 0 & 0 & \ldots & 1 \end{vmatrix} \quad \text{(A.35)}$$

since $\partial p_i/\partial p_i = 1$ and $\partial p_i/\partial p_j = 0$ (here $i \neq j$). It is thus shown that the Jacobian equals unity, and, consequently, the mean value of the kinetic energy falling to the i-th degree of freedom is determined by the expression

$$\langle \mathscr{E}_{ki} \rangle = \int \frac{1}{2} p_i \frac{\partial \mathscr{E}}{\partial p_i} e^{(F-\mathscr{E})/(kT)} dq_1 \ldots dq_{3N} dp_1 \ldots dp_{3N} \quad \text{(A.36)}$$

Let us first perform integration over p_i, having in view that the possible values of the generalized momentum range from $-\infty$ to $+\infty$. Since

$$\int\limits_{-\infty}^{+\infty} \frac{p_i}{2} \frac{\partial \mathscr{E}}{\partial p_i} e^{(F-\mathscr{E})/(kT)} dp_i = -\frac{kT}{2} \int\limits_{-\infty}^{+\infty} p_i \frac{\partial}{\partial p_i} [e^{(F-\mathscr{E})/(kT)}] dp_i$$

after integration by parts, we obtain

$$\int\limits_{-\infty}^{+\infty} \frac{p_i}{2} \frac{\partial \mathscr{E}}{\partial p_i} e^{(F-\mathscr{E})/(kT)} dp_i$$

$$= -\frac{kT}{2} p_i e^{(F-\mathscr{E})/(kT)} \Big|_{-\infty}^{+\infty} + \frac{kT}{2} \int\limits_{-\infty}^{+\infty} e^{(F-\mathscr{E})/(kT)} dp_i$$

The first term vanishes, because with an infinite value of the generalized momentum, the system's energy is also infinite, and therefore the exponential factor is infinitely small. Now (A.36) can be written as

$$\langle \mathscr{E}_{ki} \rangle = \frac{kT}{2} \int e^{(F-\mathscr{E})/(kT)} dq_1 \ldots dq_{3N} dp_1 \ldots dp_{3N}$$

i.e.,

$$\langle \mathscr{E}_{ki} \rangle = \frac{kT}{2} \qquad (A.37)$$

because according to the normalization condition, we have

$$\int e^{(F-\mathscr{E})/(kT)} dq_1 \ldots dq_{3N} dp_1 \ldots dp_{3N} = \int e^{(F-\mathscr{E})/(kT)} d\Gamma = 1$$

Formula (A.37) is exactly the mathematical form of the theorem on the uniform distribution of the kinetic energy among degrees of freedom.

In concluding, we shall note that a similar relation can be obtained for the potential energy, but for this to occur, the following conditions must be satisfied.

First, the potential energy must be a quadratic function of the generalized coordinates q_i so that

$$\mathscr{E}_p = \sum_i \frac{1}{2} q_i \frac{\partial \mathscr{E}_p}{\partial q_i} \qquad (A.38)$$

Second, the kinetic energy should not depend on the generalized coordinates so that relation (A.38) could be written as

$$\mathscr{E}_p = \sum_i \frac{1}{2} q_i \frac{\partial \mathscr{E}}{\partial q_i} \qquad (A.39)$$

Now for the mean value of the potential energy per i-th degree of freedom, i.e. for

$$\langle \mathscr{E}_{pi} \rangle = \left\langle \frac{1}{2} q_i \frac{\partial \mathscr{E}}{\partial q_i} \right\rangle$$

with a view to the Jacobian equalling unity, we find according to the general rule that

$$\langle \mathscr{E}_{pi} \rangle = \int \frac{1}{2} q_i \frac{\partial \mathscr{E}}{\partial q_i} e^{(F-\mathscr{E})/(kT)} dq_1 \ldots dq_{3N} dp_1 \ldots dp_{3N}$$

Integration is performed in the same way as in the preceding case and leads to the equation

$$\langle \mathscr{E}_{\mathbf{p}i} \rangle = \frac{kT}{2} \qquad\qquad \text{(A.40}$$

4. Transition to a Reference Frame Associated with the Centre of Mass

By (13.18), we have

$$\left. \begin{aligned} \mathbf{p}_1 &= \frac{m_1}{(m_1 + m_2)} \, \mathbf{p}_s + \mathbf{p}_r \\[2mm] \mathbf{p}_2 &= \frac{m_2}{(m_1 + m_2)} \, \mathbf{p}_s - \mathbf{p}_r \end{aligned} \right\} \qquad \text{(A.41}$$

Since

$$d\Omega_1 \, d\Omega_2 = |\, J \,| \, d\Omega_s \, d\Omega_r$$

where J is the Jacobian of the transformation from $\mathbf{p}_1$ and $\mathbf{p}_2$ to $\mathbf{p}_s$ and $\mathbf{p}_r$, it is necessary to evaluate the Jacobian. We have

$$J = \begin{vmatrix} \dfrac{\partial p_{1x}}{\partial p_{sx}} & \dfrac{\partial p_{1x}}{\partial p_{sy}} & \dfrac{\partial p_{1x}}{\partial p_{sz}} & \dfrac{\partial p_{1x}}{\partial p_{rx}} & \dfrac{\partial p_{1x}}{\partial p_{ry}} & \dfrac{\partial p_{1x}}{\partial p_{rz}} \\[3mm] \dfrac{\partial p_{1y}}{\partial p_{sx}} & \dfrac{\partial p_{1y}}{\partial p_{sy}} & \cdot & \cdot & \cdot & \cdot \cdot \cdot \cdot \cdot \cdot \cdot \\[3mm] \cdot \cdot \cdot & \cdot \cdot \cdot \cdot \cdot \cdot & \cdot \cdot \cdot \cdot \cdot \cdot & \cdot \cdot & \cdot & \cdot \\[1mm] \dfrac{\partial p_{2z}}{\partial p_{sx}} & \dfrac{\partial p_{2z}}{\partial p_{sy}} & \dfrac{\partial p_{2z}}{\partial p_{sz}} & \dfrac{\partial p_{2z}}{\partial p_{rx}} & \dfrac{\partial p_{2z}}{\partial p_{ry}} & \dfrac{\partial p_{2z}}{\partial p_{rz}} \end{vmatrix} \qquad \text{(A.42}$$

It is quite easy to calculate the relevant derivatives with the aid of (A.41). The non-zero ones are

$$\frac{\partial p_{1x}}{\partial p_{sx}} = \frac{\partial p_{1y}}{\partial p_{sy}} = \frac{\partial p_{1z}}{\partial p_{sz}} = \frac{m_1}{m_1 + m_2} \; ;$$

$$\frac{\partial p_{1x}}{\partial p_{rx}} = \frac{\partial p_{1y}}{\partial p_{ry}} = \frac{\partial p_{1z}}{\partial p_{rz}} = 1;$$

$$\frac{\partial p_{2x}}{\partial p_{sx}} = \frac{\partial p_{2y}}{\partial p_{sy}} = \frac{\partial p_{2z}}{\partial p_{sz}} = \frac{m_2}{m_1 + m_2} \; ;$$

$$\frac{\partial p_{2x}}{\partial p_{rx}} = \frac{\partial p_{2y}}{\partial p_{ry}} = \frac{\partial p_{2z}}{\partial p_{rz}} = -1$$

Substitution into (A.42) yields

$$
J = \begin{vmatrix}
\dfrac{m_1}{m_1+m_2} & 0 & 0 & 1 & 0 & 0 \\[2mm]
0 & \dfrac{m_1}{m_1+m_2} & 0 & 0 & 1 & 0 \\[2mm]
0 & 0 & \dfrac{m_1}{m_1+m_2} & 0 & 0 & 1 \\[2mm]
\dfrac{m_2}{m_1+m_2} & 0 & 0 & -1 & 0 & 0 \\[2mm]
0 & \dfrac{m_2}{m_1+m_2} & 0 & 0 & -1 & 0 \\[2mm]
0 & 0 & \dfrac{m_2}{m_1+m_2} & 0 & 0 & -1
\end{vmatrix}
\qquad (A.43)
$$

If we add the fourth row to the first one, the fifth to the second, and the sixth to the third, we obtain the following determinant whose magnitude is evidently unity:

$$
J = \begin{vmatrix}
1 & 0 & 0 & 0 & 0 & 0 \\[2mm]
0 & 1 & 0 & 0 & 0 & 0 \\[2mm]
0 & 0 & 1 & 0 & 0 & 0 \\[2mm]
\dfrac{m_2}{m_1+m_2} & 0 & 0 & -1 & 0 & 0 \\[2mm]
0 & \dfrac{m_2}{m_1+m_2} & 0 & 0 & -1 & 0 \\[2mm]
0 & 0 & \dfrac{m_2}{m_1+m_2} & 0 & 0 & -1
\end{vmatrix}
\qquad (A.44)
$$

5. List of Symbols

A	amplitude; work; work function
a	acceleration; constant; dimension
b	constant
b_0	diameter of molecule
C	capacitance; constant; heat capacity
c	specific heat capacity; speed of light in vacuum; speed of sound
D	diffusion coefficient; dispersion; drift constant
d	distance; lattice constant
E	electric field strength
$\mathscr{E}$	energy
e	charge of elementary particle

e	base of natural logarithms
erf	error function (probability integral)
F	free energy
F	force
f	distribution function; frequency
f_0	Maxwell distribution function
G	number of waves
g	acceleration of free fall; density of states
grad	gradient
H	height (altitude)
h	Planck's constant
$\hbar$	Planck's constant divided by 2π
I	current; moment of inertia
i	dummy index; number of degrees of freedom
i	current density
J	Jacobian; particle flux
j	dummy index; flux density
k	Boltzmann constant
k	wave number
L	inductance
L	vector
l	altitude; length
M	mass; total number of trials
n	number of trials
m_0	mass of particle
N	total number of particles
N_A	Avogadro's constant
n	number
n	normal vector
P	power; pressure
p	momentum
Q	amount of heat; charge
q	generalized coordinate
R	molar gas constant; radius; resistance
R_e	radiant emittance
r	radius
r_ω	spectral density of radiant emittance (emissivity)
r	position vector
S	area; entropy
$S(\omega)$	spectral density of current pulse
S.T.P.	standard temperature and pressure

s	area
s_0	effective scattering cross section
T	absolute temperature
t	time
U	internal energy; potential; potential difference; voltage
V	volume
$\mathbf{v}$	velocity
W	probability
w	probability density
Z	atomic number; state integral
Z^*	partition function (statistical sum)
z ·	altitude
α	angle
β	coefficient; rigidity coefficient of elastic force
Γ	volume of phase space
γ	fraction
Δ	increment; path difference; width
δ	increment; parameter
ε	kinetic energy of molecule; permittivity
ε_0	electric constant
η	coefficient of friction; efficiency; mobility coefficient
η'	drift coefficient
Θ	Debye temperature
θ	angle
$\varkappa$	rigidity (spring constant)
λ	free path; Lagrangian undetermined multiplier; wavelength
μ	chemical potential; Fermi level; molar mass
ν	frequency
ξ	variable
ρ	density; distance; impact parameter
σ	conductivity; Stefan-Boltzmann constant
τ	relaxation time; volume element
φ	angle; function; potential difference
χ	angle
ψ	angle; function
Ω	momentum space volume
ω	angular frequency; angular velocity

6. Values of Some Physical Constants

Speed of light (in vacuum) c	2.9979×10^8 m/s
Planck's constant h	6.6262×10^{-34} J s
$\hbar = h/2\pi$	1.0546×10^{-34} J s

Elementary charge e	1.6022×10^{-19} C
Avogadro constant N_A	6.0222×10^{23} mol^{-1}
Molar gas constant R	8.3144 J/(K mol)
Standard volume, ideal gas V_0	2.2421 m^3/mol
Boltzmann constant k	1.3806×10^{-23} J/(K mol)
Stefan-Boltzmann constant σ	5.6696×10^{-8} W/(m^2 K^4)
Electron rest mass m_e	9.1096×10^{-31} kg
Proton rest mass m	1.6726×10^{-27} kg
Neutron rest mass m	1.6749×10^{-27} kg

ADDITIONAL READING

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